Appendix A

Summary of Ambient Air Monitoring for Methyl Bromide

dpr Department of Pesticide Regulation

Paul E. Helliker
Director

Gray Davis
Governor

Winston H. Hickox
Secretary, California Environmental Protection Agency

March 30, 2001

TO: Interested Parties

SUBJECT: SUMMARY OF AMBIENT AIR MONITORING FOR METHYL BROMIDE

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) monitored for methyl bromide in two areas of the state between July and November 2000. DPR has evaluated ARB's data by comparing the measured air concentrations to target concentrations. DPR's goal is to regulate methyl bromide use so that the target concentrations are not exceeded. As described in the attached document, air concentrations for all one-day and one-week periods were below the target concentrations, but air concentrations for an eight-week period were above the target concentration.

DPR is analyzing the monitoring data as well as pesticide use patterns and weather data to determine the major factors causing the high air concentrations. Based on this analysis, DPR will develop mitigation measures to reduce air concentrations to acceptable levels. Some of the mitigation measures that DPR is investigating are limits on the amount of methyl bromide that can be applied in a given area, increasing the time or distance between methyl bromide fumigations, and increasing the size of buffer zones. We expect to discuss the options with you over the next few months. If additional mitigation measures are needed, we plan on implementing them prior to July 2001, the start of the peak use period.

DPR has requested ARB conduct additional monitoring later this year to determine the effectiveness of the mitigation measures. In addition, the monitoring will help determine if the regulations implemented in January 2001 have had any effect on methyl bromide levels in air.

For additional information concerning this monitoring or other methyl bromide issues please feel free to contact Mr. Randy Segawa, of my staff, at (916) 324-4137, rsegawa@cdpr.ca.gov, or DPR's web site, <www.cdpr.ca.gov>.

Sincerely,

John S. Sanders

John S. Sanders, Ph.D.
Environmental Monitoring Branch
(916) 324-4100

***FLEX YOUR POWER!** The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Web site at <www.cdpr.ca.gov>.*

Summary of Ambient Air Monitoring for Methyl Bromide
March 28, 2001

BACKGROUND

Methyl bromide is one of the most widely used pesticides in California, with approximately 15 million pounds applied annually in the state. Methyl bromide is a gaseous fumigant that kills insects, mites, rodents, nematodes, termites, weeds, and organisms that cause plant diseases. Because it is a colorless, odorless gas, methyl bromide is normally mixed with chloropicrin, a tear gas with a noticeable odor.

Farmers use methyl bromide to treat soil before planting vegetable, fruit and nut crops, and flower and forest nurseries. Depending on the crop, field applications may occur annually, or once every several years. Methyl bromide is injected into the soil with specialized application equipment. After harvest, methyl bromide fumigation protects crops from pest damage during storage and transportation. The fumigant is also used for termite eradication in homes and other structures, and to control insects in mills, ships, railroad cars and other transportation vehicles.

The Department of Pesticide Regulation (DPR) and the county agricultural commissioners have implemented extensive restrictions on the use of methyl bromide, such as buffer zones surrounding treated fields, equipment and procedures for application, worker safety requirements, and notification to people near fumigated fields.

As required by state law, DPR evaluates, identifies, and controls pesticides as toxic air contaminants. Under this program, methyl bromide was identified as a toxic air contaminant in 1996. As part of the toxic air contaminant program, the Air Resources Board (ARB) monitors for pesticides under the direction of DPR. ARB conducted ambient air monitoring for methyl bromide in 2000. DPR requested this monitoring as part of an ongoing effort to evaluate seasonal exposures to methyl bromide and determine if current restrictions provide adequate safety for people who live and work in areas where fumigations occur to multiple fields. This document summarizes the monitoring results and preliminary risk evaluation.

SAMPLING PLAN

Monitoring was conducted within the areas and periods of most use. ARB monitored six locations in Kern County from July 19 to September 1, 2000 (Figure 1). At each location, 1-day samples were collected four days per week for seven weeks. ARB monitored six locations in the Monterey and Santa Cruz area from September 11 to November 3, 2000 (Figure 2). At each location, 1-day samples were collected four days per week for eight weeks. Additional samples were collected for quality control.

RESULTS

The results are summarized in Table 1, and the complete results are given in Appendix A. All but one of the 320 samples contained a detectable and quantifiable amount of methyl bromide (detection limit 0.002 parts per billion [ppb], quantitation limit 0.01 ppb). *See Appendix B for an explanation of terminology, such as detection limit and parts per billion.* The highest 1-day concentration detected was 30.8 ppb. The highest 1-week average concentration was 15.5 ppb. The highest average concentration for the study period (7 or 8 weeks) was 7.7 ppb.

EVALUATION OF HEALTH RISKS

Methyl bromide causes a variety of health effects in experimental animals and humans. To evaluate health risks, DPR has calculated target concentrations or goals based on the toxic properties of methyl bromide, and compared the target concentrations to the monitoring data. These target concentrations are generally 100 times lower than doses that do not cause adverse effects, or the no-observed effect level (NOEL) in animal studies, adjusting for breathing rate differences between animals and humans. The 100-fold factor accounts for variation in sensitivity between individuals and assumes that people are more sensitive than experimental animals to the effects of methyl bromide. For a 1-day average exposure, the target concentration is 250 ppb for children and 210 ppb for adults (the target concentration for a child is higher than an adult in this case). For a 1-week average exposure, the target concentration is 70 ppb for children and 120 ppb for adults. For an 8-week average exposure, the target concentration is 1 ppb for children and 2 ppb for adults.

DPR's goal is to regulate methyl bromide use so that the target concentrations are not exceeded. The air concentrations for all 1-day and 1-week periods were lower than the target concentrations, but air concentrations exceeded the target concentration over a 7 to 8-week period (Table 1). For the location with the highest concentration, the 8-week exposure was almost eight times the target level.

While the 8-week target concentration was exceeded in several locations, illnesses would not be expected to occur because the target concentration incorporates a 100-fold safety factor.

PRELIMINARY CONCLUSIONS

Monitoring was conducted during the high methyl bromide use period of July 19 to September 1 in Kern county, and September 11 to November 3 in Monterey and Santa Cruz counties.

Monitoring was conducted in two areas of the highest methyl bromide use.

The 1-day air concentrations of methyl bromide met DPR's goal (i.e., lower than the 1-day target concentration) at all locations.

The 1-week air concentrations of methyl bromide met DPR's goal (i.e., lower than the 1-week target concentration) at all locations.

The average air concentrations of methyl bromide for the 7 to 8-week study period did not meet DPR's goal (i.e., greater than the 8-week target concentration) at one of the six monitoring locations in Kern County and at four of the six monitoring locations in the Monterey/Santa Cruz area.

FUTURE ACTIVITIES

DPR is currently analyzing the data to determine whether application patterns, weather, or other factors played a role in ambient air levels. DPR expects to finalize its analysis this spring, and if additional restrictions are deemed necessary, DPR intends to take action before the high-use season begins.

DPR has requested that ARB conduct additional ambient air monitoring for methyl bromide in these same areas in 2001 since it can be accomplished simultaneously with other planned monitoring. Additionally, the monitoring will show the change in air concentrations due to new methyl bromide regulations implemented in January 2001.

ADDITIONAL INFORMATION

This summary is based on the following documents.

ARB, 2000. Final Report for the 2000 Methyl Bromide and 1,3-Dichloropropene Air Monitoring in Kern County. California Air Resources Board, Sacramento, CA.

ARB, 2001. Final Report for the 2000 Methyl Bromide and 1,3-Dichloropropene Air Monitoring in Monterey and Santa Cruz Counties. California Air Resources Board, Sacramento, CA.

DPR, 1999. Methyl Bromide Risk Characterization Document for Inhalation Exposure (DRAFT RCD 99-02). California Department of Pesticide Regulation, Sacramento, CA.

Lim, 2001. Evaluation of Ambient Air Concentration of Methyl Bromide in Monterey, Santa Cruz, and Kern Counties. Memorandum from Lori Lim to Gary Patterson, Medical Toxicology Branch, February 15, 2001. California Department of Pesticide Regulation, Sacramento, CA.

Powell, 2001. Exposures to methyl bromide based on ARB 2000 monitoring in Monterey/Santa Cruz and Kern Counties. Memorandum from Sally Powell to Joe Frank, Worker Health and Safety Branch, February 9, 2001. California Department of Pesticide Regulation, Sacramento, CA.

Figure 1.

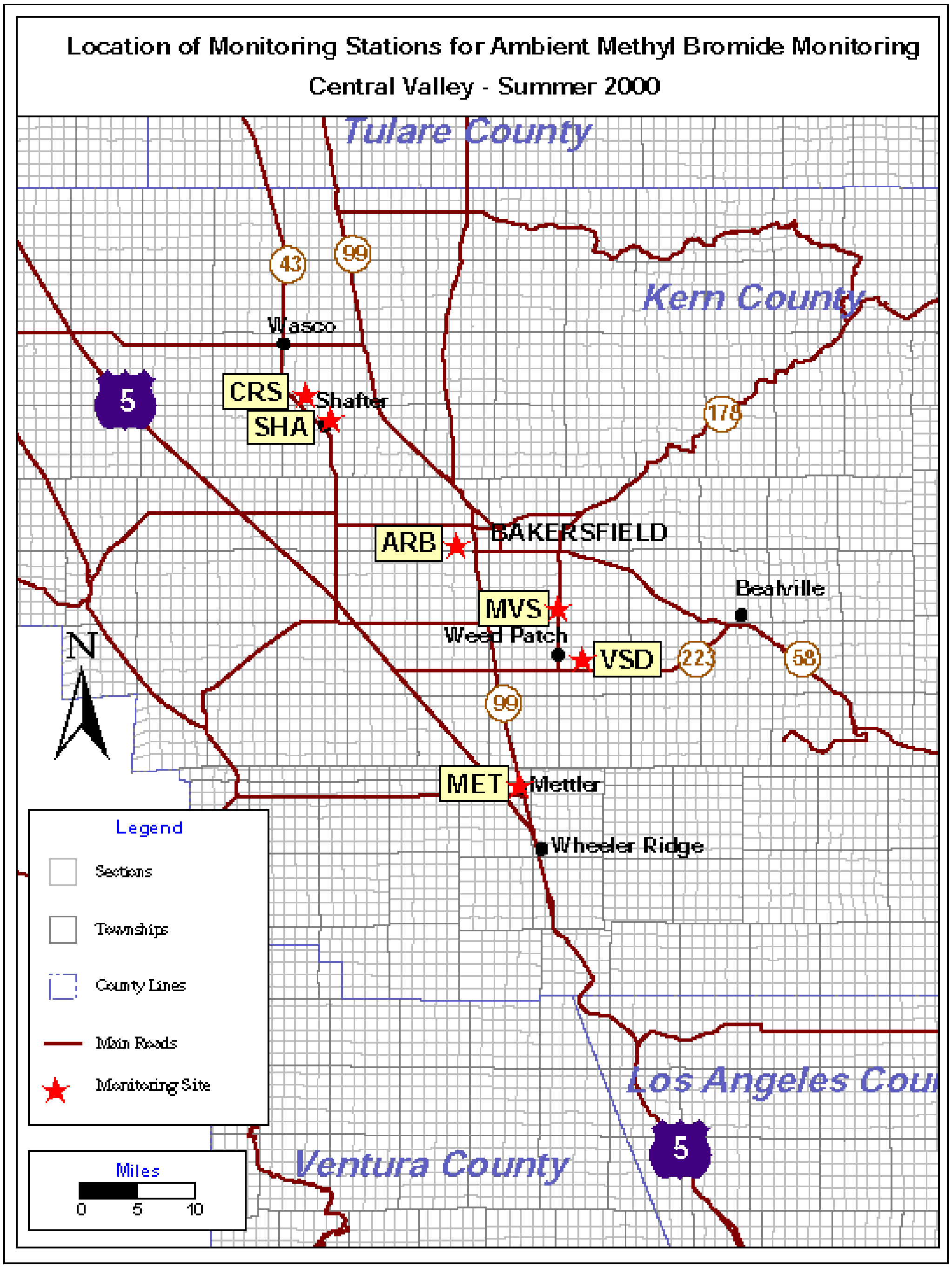
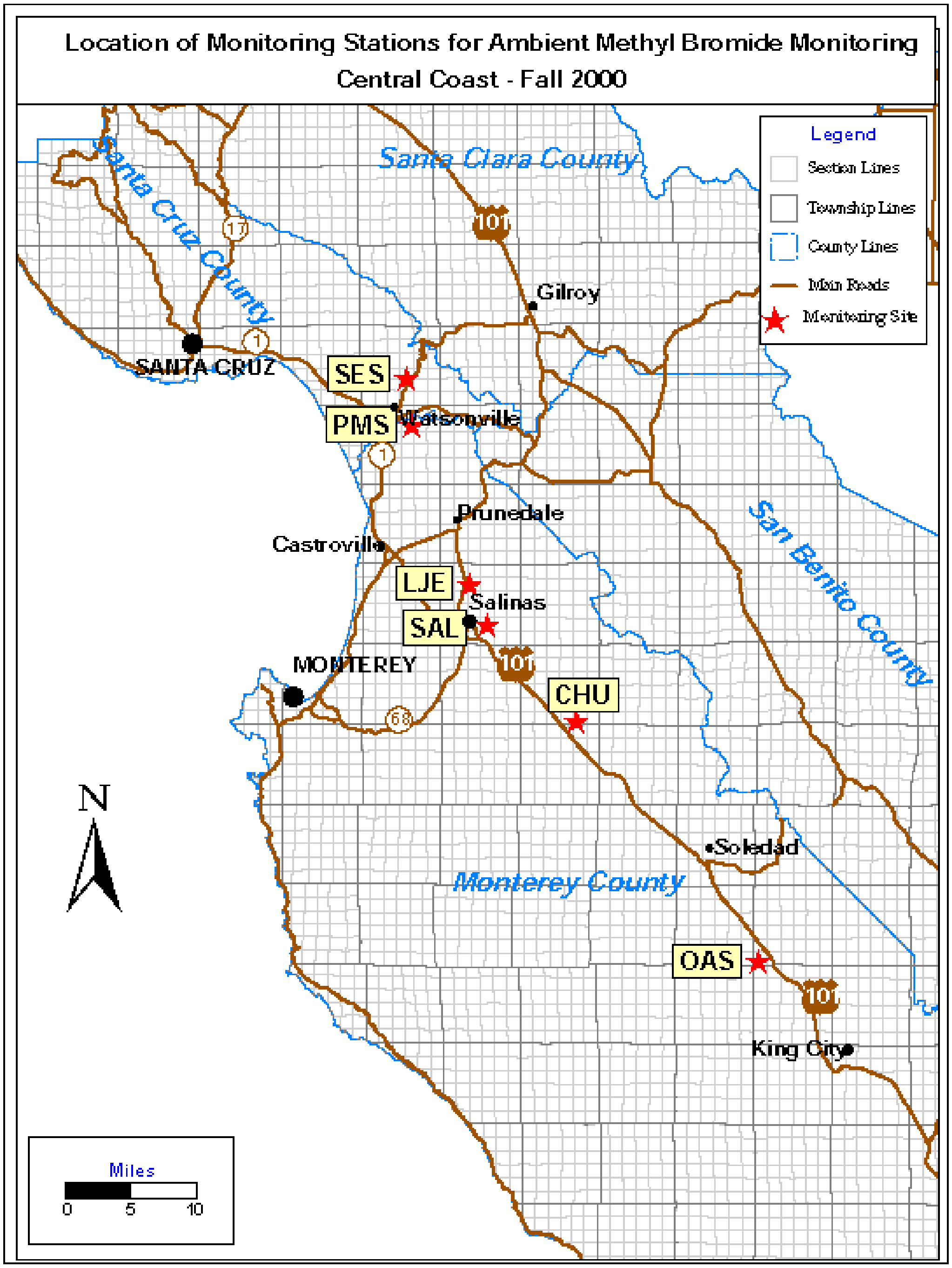

Location of Monitoring Stations for Ambient Methyl Bromide Monitoring
Central Valley - Summer 2000
Tulare County
Kern County
Los Angeles Cou
Ventura County
Wasco
Shafter
CRS
SHA
ARB
BAKERSFIELD
MVS
Weed Patch
VSD
Bealville
MET
Mettler
Wheeler Ridge
43
99
178
223
58
5
N
Legend
Sections
Townships
County Lines
Main Roads
Monitoring Site
Miles
0
5
10

Figure 2.



Location of Monitoring Stations for Ambient Methyl Bromide Monitoring
Central Coast - Fall 2000
Legend
Section Lines
Township Lines
County Lines
Main Roads
Monitoring Site
Santa Clara County
Santa Cruz County
San Benito County
Monterey County
SANTA CRUZ
Gilroy
Watsonville
Prunedale
Castroville
Salinas
MONTEREY
Soledad
King City
SES
PMS
LJE
SAL
CHU
OAS
101
17
1
68
N
Miles
0
5
10

Table 1. Summary of methyl bromide air monitoring results.

Location	Highest 1-Day Concentration (ppb)	Highest 1-Week Concentration (ppb)	Average Concentration for Study Period (ppb)
Monterey and Santa Cruz Counties, Sep 11 - Nov 3, 2000			
CHU Chualar School, Chualar, CA	2.4	1.6	0.6
LJE La Joya Elementary School, Salinas, CA	24.0	11.1	3.8
OAS Oak Avenue School, Greenfield, CA	1.8	1.0	0.4
PMS Pajaro Middle School, Watsonville, CA	30.8	15.5	7.7
SAL Ambient Monitoring Station, Salinas, CA	7.9	3.0	1.3
SES Salsepuedes Elementary School, Watsonville, CA	16.4	8.3	2.6
Kern County, Jul 19 - Sep 1, 2000			
ARB Ambient Monitoring Station, Bakersfield, CA	1.0	0.5	0.2
CRS Cotton Research Station, Shafter, CA	14.2	4.6	2.2
MET Mettler-Fire Station, Mettler, CA	0.2	0.1	0.08
MVS Mountain View School, Lamont, CA	0.5	0.2	0.09
SHA Shafter-Walker Ambient Monitoring Station, Shafter, CA	3.5	1.8	0.8
VSD Vineland School District, Bakersfield, CA	0.3	0.2	0.1
Target Concentrations[a]			
Child	*250*	*70*	*1*
Adult	*210*	*120*	*2*

[a] DPR uses target concentrations as benchmarks for its regulatory program. DPR establishes and modifies its restrictions so that the target concentrations should not be exceeded. Target concentrations are based on no-observed-effect levels established from animal tests of various exposure periods with a safety factor of 100x.

APPENDIX A
RESULTS OF EACH SAMPLE

Table 2. Methyl bromide results from Kern County (ppb)

Sample Start Date	Monitoring Locations[1]					
	ARB	CRS	MET	MVS	SHA	VSD
07/19/00	0.02	ND[2]	0.02	0.02	0.02	0.02
07/19/00	0.02	ND	0.11	0.02	0.03	0.02
07/20/00	1.00	5.66	0.11	0.10	3.53	0.21
07/24/00	0.18	3.11**	0.08	0.05**	0.63	0.06
07/25/00	0.34	0.89	0.03**	0.05**	0.36	0.04**
07/26/00	0.05**	1.43	0.11	0.08**	0.67	0.06
07/26/00	0.07**	1.45	0.21	0.07	0.66	0.06**
07/27/00	0.18	9.14	0.22	0.21	1.17	0.23
07/31/00	0.06**	1.61	0.19**	0.07	0.81	0.12**
08/01/00	0.93	1.72	0.12	0.08	1.15	0.12
08/02/00	0.11	0.86**	0.08**	0.06**	0.63	0.07**
08/02/00	0.11	0.85	0.08	0.06	0.62	0.07
08/03/00	0.07	14.18	0.06**	0.05	0.66	0.06
08/07/00	0.22	0.60	0.04	0.03	0.16	0.03
08/08/00	0.10	0.24	0.05	0.09	0.19**	0.09
08/09/00	0.10	0.09	0.05	0.05	0.09	0.07
08/09/00	0.10	0.09	0.05	0.05**	0.08	0.07
08/10/00	0.19	0.91	0.14	0.21	0.90	0.23
08/14/00	0.03	0.06	0.03	0.03	0.06	0.03
08/15/00	0.08	0.24**	0.04	0.05	0.06	0.05
08/16/00	0.01	NS[3]	0.01**	0.01	0.02**	0.01
08/16/00	0.02	NS	0.02	0.02**	0.02	0.01
08/17/00	0.04	NS	0.03	0.04	0.04	0.04
08/21/00	0.03	0.05	0.03	0.03	0.46	0.03
08/22/00	0.03	0.07	0.05	0.03	0.07	0.04
08/23/00	0.11	1.38	0.07	0.07	0.35	0.07
08/23/00	0.11	1.32	0.03**	0.07**	0.38	0.07
08/24/00	NA	1.07	0.09	0.24	0.49	0.19
08/28/00	0.31	2.69	0.19	0.49	2.83	0.35
08/29/00	0.10	4.88	0.09	0.09	1.02	0.10
08/30/00	0.26	2.59	0.22	0.16	1.84	0.18
08/30/00	0.25	2.66	0.22**	0.16**	1.86	0.18
08/31/00	0.09	0.94	0.07	0.07	0.42	0.06

[1] See Table 1 for description of monitoring locations
[2] None Detected, detection limit 0.002 ppb
[3] No Sample
**Sample air flow rate deviation was >25%, not used to calculate averages

Table 3. Methyl bromide results (ppb) from Monterey and Santa Cruz Counties

Sample Start Date	Monitoring Locations[1]					
	CHU	LJE	OAS	PMS	SAL	SES
09/11/00	0.67	5.57	0.31	5.08	1.98	9.46
09/12/00	0.81	24.03	0.70	10.10	2.14	16.43
09/12/00	NS[2]	NS	0.28	NS	NS	NS
09/13/00	0.94	7.32	0.68	1.11	1.50	2.62**
09/13/00	0.88	8.41	NS	1.12	1.46	NS
09/14/00	0.50	4.52	0.22	4.39	0.97	4.54
09/14/00	NS	NS	NS	NS	NS	4.86
09/18/00	0.58	11.08	0.42	11.22	1.45	3.93**
09/19/00	2.16	11.85	0.65	15.46	3.50	7.22
09/20/00	0.71	1.57	0.63	1.99	1.77	0.16
09/20/00	1.63**	2.48	0.54	1.30	1.49	0.14
09/21/00	0.84	NS	0.06	3.88	2.74	0.21
09/25/00	0.12	0.30	0.12**	1.24	0.15	1.22
09/26/00	0.32	0.60	0.15	2.73	0.26	0.82
09/26/00	0.33**	0.79**	0.16	3.57	NS	0.80
09/27/00	0.23	0.27	0.25	13.29	0.08	1.69
09/28/00	0.68	3.71	0.16	21.48	2.58	4.12
10/02/00	0.37	0.20	0.29	0.78	0.19	0.97
10/03/00	0.31	0.13	0.42	1.14	0.09	0.48
10/03/00	0.31	0.12	NS	0.91	0.09	0.48
10/04/00	0.61	4.26	0.34	1.26	1.08	0.44
10/04/00	NS	NS	0.34	NS	NS	NS
10/05/00	0.31	0.81	0.55	1.90	0.65	2.29
10/10/00	0.07	0.69	0.12**	5.45	0.06**	0.96
10/10/00	NS	NS	NS	NS	NS	1.07
10/11/00	0.38	0.62	0.33	13.12	0.38	0.52
10/11/00	0.05**	0.25**	NS	12.54**	0.39	NS
10/12/00	0.33	1.20	0.28	28.18	1.65	0.92
10/12/00	NS	1.13	0.29	NS	NS	NS
10/16/00	2.41	10.75	0.90	22.27	7.91	3.24**
10/16/00	NS	13.16	0.94	23.03**	NS	3.28
10/17/00	NA	2.13	0.70	3.94	1.21	2.95
10/17/00	1.29	NS	NS	NS	NS	NS
10/18/00	1.21	3.53	0.70	6.86	0.78	4.76
10/18/00	NS	NS	NS	NS	0.81	NS
10/19/00	1.54	3.69	1.84	4.15	2.12	3.53
10/23/00	1.14	7.04	0.62	30.77	2.38	3.28
10/24/00	0.57	1.25**	0.59	8.45	1.23	1.20
10/25/00	0.30	0.77	0.22	3.06	0.64	2.11
10/25/00	0.30	0.79	0.23	2.89	0.65	2.23
10/26/00	0.34	1.26	0.12	2.55	0.55	1.32
10/30/00	0.11	0.20	0.07	0.54	0.10	0.08
10/31/00	0.11	0.31	0.10	1.78	0.13	0.27
11/01/00	0.09	0.20	0.07	1.71	0.14	0.16
11/01/00	0.08	0.20	0.06	1.74	0.14	0.16
11/02/00	0.11	0.30	0.08	0.38	0.19	0.36

[1] See Table 1 for description of monitoring locations
[2] No Sample
**Sample air flow rate deviation was >25%, not used to calculate averages

APPENDIX B
EXPLANATION OF TERMINOLOGY

Concentration: The amount of a chemical in air is normally expressed as a concentration, the amount of the chemical in a given amount of air. Concentrations in air can be expressed in many different units, the same way that distance can be expressed as inches, feet, meters, or miles. Concentrations in air can be expressed in units of volume or weight. One common unit is percent volume. For example, air contains 21 percent oxygen. This means in 100 cubic meters of air, 21 cubic meters is comprised of oxygen.

Concentration Units and Conversion Factors: DPR often expresses methyl bromide air concentrations in parts per billion (ppb). Similar units are parts per million (ppm) and percent (percent is synonymous with parts per hundred). These units are all ratios or proportions and refer to the volume of a chemical in a volume of air. For example, 1,000 ppb means that 1,000 cubic meters of methyl bromide is contained in 1 billion cubic meters of air. While it may seem counterintuitive because a billion is more than a million, 1 ppm is a concentration 1000 times greater than 1 ppb.

ARB's report expresses the methyl bromide air concentrations as nanograms per cubic meter (ng/m^3). This refers to the amount (weight) of methyl bromide in a volume of air. For example, 1,000 ng/m^3 means 1,000 nanograms of methyl bromide is contained in one cubic meter of air.

The conversion factor from nanograms per cubic meter to parts per billion is not straightforward because it is usually different from chemical to chemical. For methyl bromide, the concentration in nanograms per cubic meter should be divided by 3,880 to convert to parts per billion. For example, 388,000 ng/m^3 divided by 3,880 equals 100 ppb. The following table summarizes these conversion factors.

Change From	To	
ng/m^3	ppb	divide by 3,880
ppb	ng/m^3	multiply by 3,880
ppb	ppm	divide by 1,000
ppm	ppb	multiply by 1,000

Detection Limit: The detection limit is the smallest amount of the chemical that can be identified in a sample with the method employed. For example, a detection limit of 0.002 ppb for methyl bromide means that a sample can be identified as containing methyl bromide if the concentration is at least 0.002 ppb. If the sample contains no methyl bromide, or methyl bromide at a concentration less than 0.002 ppb, the sample is designated as containing no detectable amount. When calculating average concentrations or other statistics, samples with no detectable amount are normally assumed to have a concentration of one-half the detection limit. For example, if the detection limit is 0.002 ppb, samples with no detectable amount are assumed to have 0.001 ppb. The detection limit is a characteristic of both the method and the chemical. Different methods can have different detection limits for the same chemical. The same method can have different detection limits for different chemicals. See also quantitation limit.

No-Observed-Effect Level, NOEL: The NOEL is the lowest experimental concentration for which no adverse health effects were documented in a toxicology test. For example, a NOEL of 2000 ppb means that test subjects (usually animals) exposed to 2000 ppb had no adverse health effects for the duration of the test. Adverse effects occurred at the next highest dose of the test. The health or toxic effects of a chemical are related to the amount of chemical absorbed by the body. The more chemical absorbed by the body the greater the toxic effects. Scientists often say that the dose makes the poison, or stated another way, there are no poisons only poisonous doses. The NOEL is usually different for each chemical. Also, the NOEL is usually different for different exposure periods. Normally, the longer the exposure period, the lower the NOEL. In other words, it takes less chemical to produce an adverse effect if exposure occurs for one year, than if exposure occurs for one day.

Parts Per Billion, ppb: See Concentration Units and Conversion Factors.

Quantitation Limit: Similar to detection limit, the quantitation limit is the smallest amount of the chemical that can be measured. For example, a quantitation limit of 0.01 ppb for methyl bromide means that the concentration can be measured if the sample contains at least 0.01 ppb of methyl bromide. Samples with concentrations less than the quantitation limit, but more than detection limit can be identified as containing methyl bromide, but the concentration cannot be measured reliably with the method employed. For example, if the detection limit is 0.002 ppb and the quantitation limit is 0.01 ppb, samples with concentrations at least 0.01 ppb can be measured, samples with concentrations between 0.002 and 0.01 ppb contain an unmeasurable concentration between 0.002 and 0.01 ppb, and samples with concentrations less than 0.002 ppb are designated as containing no detectable amount. When calculating average concentrations or other statistics, samples with an unmeasurable concentration are normally assumed to have a concentration of the midpoint between the detection limit and the quantitation limit. For example, if the detection limit is 0.002 ppb and the quantitation limit is 0.01 ppb, samples with an unmeasurable amount are assumed to have 0.006 ppb. As with the detection limit, the quantitation limit is a characteristic of both the method and the chemical. Different methods can have different quantitation limits for the same chemical. The same method can have different quantitation limits for different chemicals.

Target Concentration: The target concentration is the benchmark or goal that DPR does not want to exceed. The target concentration is not a legal standard, but a goal for DPR's regulatory program. For example, if the target concentration for methyl bromide is 2 ppb, DPR implements restrictions on the use of methyl bromide (examples: buffer zones or acreage limitations) so that people's exposure should not exceed 2 ppb. The target concentration is based on the no-observed effect level and incorporates a safety factor. Scientists often refer to this target concentration as the reference concentration.

Appendix B

Evaluation of Ambient Air Concentration of Methyl Bromide In Monterey, Santa Cruz, and Kern County

Paul E. Helliker
Director

Gray Davis
Governor

Winston H. Hickox
Secretary, California Environmental Protection Agency

MEMORANDUM

TO: Gary Patterson
Supervising Toxicologist, Branch Chief
Medical Toxicology Branch

FROM: Lori O. Lim
Staff Toxicologist
(916) 324-3515

Lori Lim

DATE: February 15, 2001

SUBJECT: Evaluation of Ambient Air Concentration of Methyl Bromide in Monterey, Santa Cruz, and Kern Counties

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The potential risk from exposure to ambient methyl bromide air concentrations in Monterey, Santa Cruz, and Kern Counties were evaluated. The risk was expressed as the margin of exposure (MOE) which is the ratio of the No-Observed-Effect Level (NOEL) and the estimated human exposure level. The NOELs for threshold effects were derived from animal toxicity studies as discussed in the draft Methyl Bromide Risk Characterization Document for Inhalation Exposure (DPR, 1999). The human equivalent NOELs[1] were: 21 ppm and 25 ppm, respectively, for adult and children acute exposures; 12 ppm and 7 ppm, respectively, for adult and children 1-week exposures; and 0.2 ppm and 0.1 ppm, respectively, for adult and children 6-week exposures (Table 15 of the DRAFT RCD). The exposure estimates were provided by the Worker Health and Safety Branch (Powell, 2001) and were based on studies conducted by the Air Resources Board at those counties (ARB, 2000 and 2001).

For these three counties, the highest ambient methyl bromide levels were measured at Pajaro Middle School (PMS, Watsonville, CA) for Monterey/Santa Cruz Counties and the Cotton Research Station (CRS, Shafter, CA) for Kern County. Consequently, the MOEs for all durations of exposure at these sites were lower than those for other sites.

For acute exposures, MOEs were all greater than 100 for exposure to either the maximum daily level or the 95th percentile of the daily levels (Table 1). For adults, the MOEs ranged from 682 (PMS/Monterey-Santa Cruz Counties and maximum daily level) to >93,000 (MET/Kern County site and maximum daily level). For children, the MOEs ranged from 812 (PMS site and maximum daily level) to >111,000 (MET/Kern County site and maximum daily level).

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[1] Human equivalent NOELs were calculated by accounting for respiration rate differences between human (adult and child) and experimental animals and amortized for daily exposure (Appendix G of DPR, 1999). The respiration rates were: 0.46 m^3/kg/day (child), 0.26 m^3/kg/day (adult), 0.54 m^3/kg/day (rabbit), and 0.39 m^3/kg/day (dog).

$$\text{Human equivalent NOEL (ppm)} = \text{Animal NOEL (ppm)} \times \frac{\text{animal respiration rate}}{\text{human respiration rate}} \times \frac{\text{hours exposed}}{\text{24 hours}} \times \frac{\text{days exposed per week}}{\text{7 days}}$$

For 1-week exposures, the MOEs were also greater than 100 for exposure to either the maximum weekly means or the 95th percentile of the weekly means (Table 2). For adults, the MOEs ranged from 702 (PMS/Monterey-Santa Cruz Counties and 95th percentile weekly mean level) to >82,000 (MET/Kern County site and maximum weekly level). For children, the MOEs ranged from 409 (PMS site and 95th percentile weekly means) to >48,000 (MET/Kern County site and maximum daily level).

For 8-week exposures, the MOEs were greater than 100 only at two sites (CHU and OAS) for Monterey/Santa Cruz Counties and all but CRS for Kern county (Table 3). For Monterey/Santa Cruz Counties, sites with MOEs of less than 100 were LJE (53 and 26 for adults and children, respectively), PMS (26 and 13 for adults and children, respectively), SAL (78 for children), and SES (77 and 38 for adults and children, respectively). For Kern County, the lowest MOEs were those for CRS (93 for adults and 46 for children).

In the evaluation of these MOEs, a benchmark of 100 could be considered adequate for protection of humans against potential toxicity of methyl bromide which was determined by animal studies. This benchmark of 100 included an uncertainty factor of 10 for interspecies extrapolation and a factor of 10 for intraspecies variability. These uncertainty factors assumed that the average human is 10 times more sensitive to the effects of a chemical than the most sensitive laboratory animal, and that a sensitive individual is 10 times more susceptible than an average individual. In the review of the draft RCD (DPR, 1999), the National Research Council determined that an additional uncertainty factor for potential increased sensitivities of infants and children was not needed (National Research Council, 2000).

The MOEs should also be viewed within the context of the limitations and uncertainties in the exposure calculation and the NOEL determination. The exposure calculations were based on limited monitoring data for 6 sites for each county over a few weeks. The representativeness of the data and the relationship between use and monitored levels are not known at this time (Powell, 2001). The uncertainities associated with the selection of the NOEL have been discussed in the RCD (DPR, 1999). The NOELs were based on the most sensitive endpoints and species and there were no human studies. In the absence of data, the use of a default 10-fold factor to determine the estimated subchronic NOEL from a Lowest-Observed-Effect Level (LOEL) was considered appropriate

<u>Conclusion:</u>
The acute and 1-week exposures to ambient methyl bromide levels at all sites could be considered acceptable since the MOEs were greater than 100. However, the MOEs for subchronic exposures were less than 100 in LJE, PMS, SAL (children exposure only) and SES sites in Monterey/Santa Cruz Counties, and CRS in Kern County.

cc. Keith Pfeifer

Table 1: The margins of exposure for acute exposure to monitored methyl bromide concentrations in Monterey, Santa Cruz, and Kern Counties.

Sites[a]	Maximum 24-hour level			95th percentile of daily levels		
	Exposure[b] (ppb)	Adult MOE[c]	Child MOE[c]	Exposure[b] (ppb)	Adult MOE[c]	Child MOE[c]
Monterey and Santa Cruz Counties						
CHU Chualar School, Chualar, CA	2.41	8714	10373	2.26	9292	11062
LJE La Joya Elementary School, Salinas, CA	24	875	1042	18.5	1135	1351
OAS Oak Avenue School ,Greenfield, CA	1.84	11413	13587	1.21	17355	20661
PMS Pajaro Middle School, Watsonville, CA	30.8	682	812	30.2	695	828
SAL Ambient Monitoring Station, Salinas, CA	7.91	2655	3161	6.17	3404	4052
SES Salsepuedes Elementary School, Watsonville, CA	16.4	1280	1524	12.2	1721	2049
Kern County						
ARB Ambient Monitoring Station, Bakersfield, CA	0.996	21084	25100	0.556	37770	44964
CRS Cotton Research Station, Shafter, CA	14.2	1479	1761	25.4	827	984
MET Mettler-Fire Station, Mettler, CA	0.224	93750	111607	0.239	87866	104603
MVS Mountain View School, Lamont, CA	0.487	43121	51335	0.262	80153	95420
SHA Shafter-Walker Ambient Monitoring Station, Shafter, CA	3.52	5966	7102	3.98	5276	6281
VSD Vineland School District, Bakersfield, CA	0.347	60519	72046	0.292	71918	85616

a/ Details about each site are in ARB, 2000 and 2001.

b/ Acute exposure was the highest or the 95th percentile of all single-day samples for each site (Powell, 2001).

c/ The margins of exposures (MOEs) for adults were based on an acute human equivalent No-Observed-Effect Level (NOEL) of 21 ppm derived from a NOEL of 40 ppm for developmental toxicity observed in rabbits (Breslin *et al.*, 1990). The MOEs for children were based on acute human equivalent NOEL of 25 ppm derived from a NOEL of 103 ppm for neurotoxicity in dogs (Newton, 1994).

Table 2: The margins of exposure for 1-week exposure to monitored methyl bromide concentrations in Monterey, Santa Cruz, and Kern Counties.

Sites[a]	Maximum weekly mean level			95th percentile of weekly mean levels		
	Exposure[b] (ppb)	Adult MOE[c]	Child MOE[c]	Exposure[b] (ppb)	Adult MOE[c]	Child MOE[c]
Monterey and Santa Cruz Counties						
CHU Chualar School, Chualar, CA	1.61	7453	4348	1.63	7362	4294
LJE La Joya Elementary School, Salinas, CA	10.5	1143	667	11.1	1081	631
OAS Oak Avenue School ,Greenfield, CA	1.01	11881	6931	0.918	13072	7625
PMS Pajaro Middle School, Watsonville, CA	15.5	774	452	17.1	702	409
SAL Ambient Monitoring Station, Salinas, CA	3.01	3987	2326	3.14	3821	2229
SES Salsepuedes Elementary School, Watsonville, CA	8.3	1446	843	7.45	1611	940
Kern County						
ARB Ambient Monitoring Station, Bakersfield, CA	0.507	23669	13807	0.507	23669	13807
CRS Cotton Research Station, Shafter, CA	4.59	2614	1525	5.54	2166	1264
MET Mettler-Fire Station, Mettler, CA	0.145	82759	48276	0.163	73620	42945
MVS Mountain View School, Lamont, CA	0.201	59701	34826	0.195	61538	35897
SHA Shafter-Walker Ambient Monitoring Station, Shafter, CA	1.77	6780	3955	2.05	5854	3415
VSD Vineland School District, Bakersfield, CA	0.175	68571	40000	0.181	66298	38674

a/ Details about each site are in ARB, 2000 and 2001.
b/ One-week exposure levels were the 95th percentile of weekly means for each site (Powell, 2001).
c/ The margins of exposures (MOEs) were based on a No-Observed-Effect Level (NOEL) of 20 ppm for neurotoxicity observed in pregnant rabbits (Sikov *et al.*, 1981). The human equivalent NOELs for this study were 12 ppm and 7 ppm for adults and children, respectively.

Table 3: The margins of exposure for subchronic exposure to monitored methyl bromide concentrations in Monterey, Santa Cruz, and Kern Counties.

Sites[a]	Mean of weekly means		
	Exposure[b] (ppb)	Adult MOE[c]	Child MOE[c]
Monterey and Santa Cruz Counties			
CHU Chualar School, Chualar, CA	0.644	311	155
LJE La Joya Elementary School, Salinas, CA	3.79	53	26
OAS Oak Avenue School ,Greenfield, CA	0.387	517	258
PMS Pajaro Middle School, Watsonville, CA	7.68	26	13
SAL Ambient Monitoring Station, Salinas, CA	1.29	155	78
SES Salsepuedes Elementary School, Watsonville, CA	2.6	77	38
Kern County			
ARB Ambient Monitoring Station, Bakersfield, CA	0.189	1058	529
CRS Cotton Research Station, Shafter, CA	2.16	93	46
MET Mettler-Fire Station, Mettler, CA	0.084	2381	1190
MVS Mountain View School, Lamont, CA	0.092	2174	1087
SHA Shafter-Walker Ambient Monitoring Station, Shafter, CA	0.792	253	126
VSD Vineland School District, Bakersfield, CA	0.099	2020	1010

a/ Details about each site are in ARB, 2000 and 2001.

b/ Eight-week exposure levels were the mean of the weekly means for each site (Powell, 2001).

c/ The margins of exposures (MOEs) were based on an estimated No-Observed-Effect Level (NOEL) of 0.5 ppm for neurotoxicity in dogs with a LOEL of 5 ppm (Newton, 1994). The human equivalent NOELs for this study were 0.2 ppm and 0.1 ppm for adults and children, respectively.

References:

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Powell, 2001. Exposures to methyl bromide based on ARB 2000 monitoring in Monterey/Santa Cruz and Kern Counties. Memorandum from Sally Powell to Joe Frank, Worker Health and Safety Branch, February 9, 2001. Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA.

Paul E. Helliker
Director

MEMORANDUM

Gray Davis
Governor

Winston H. Hickox
Secretary, California Environmental Protection Agency

TO: Joe Frank, Senior Toxicologist
Worker Health and Safety Branch

FROM: Sally Powell, Senior Environmental Research Scientist Sally Powell
Worker Health and Safety Branch
(916) 445-4248

DATE: February 9, 2001

SUBJECT: EXPOSURES TO METHYL BROMIDE BASED ON ARB 2000 MONITORING IN MONTEREY/SANTA CRUZ AND KERN COUNTIES

Methods

Before calculating the exposures, one-half the detection limit was substituted for two Kern County samples that were below the detection limit. (No samples in Monterey/Santa Cruz were below the quantitation limit.) The detection limit for methyl bromide was 7.1 ng/m^3 (0.00182 ppb). Further, where there were pairs of colocated samples for the same day, the two values were averaged.

All exposures are expressed as air concentrations in ppb.

Acute (24-hr) exposure

For each monitoring site separately, the maximum and the 95th percentile of all daily (24-hr) monitoring samples are given. The 95th percentile is calculated using lognormal methods:

$$95^{th}\ \%\text{ile} = \exp\{\text{arithmetic mean of log concentrations} + t_{(.95;\,n-1)} * (\text{sd of logs})\}.$$

Short-term (7-day) exposure

For each monitoring site separately, the maximum and the 95th percentile of the weekly mean concentrations are given. Each weekly mean is calculated as the arithmetic mean of the 2, 3 or 4 24-hr samples taken at a site during the week (i.e., nonmonitoring days are ignored). The 95th percentile of weekly mean concentrations is calculated using normal methods:

$$95^{th}\ \%\text{ile} = \text{arithmetic mean of week means} + t_{(.95;\,n-1)} * (\text{sd of week means}).$$

Seasonal (7- or 8-week) exposure

For each monitoring site separately, seasonal exposure is the mean concentration over the monitoring period. It is calculated as the arithmetic mean of the 8 (7 in Kern Co.) weekly means calculated as above for 7-day exposure.

Results

Plots of 24-hr concentrations by day at each site are attached. Acute, short-term and seasonal concentrations are presented in Table 1.

Table1. Methyl bromide concentrations (ppb) based on ARB 2000 monitoring in Monterey/Santa Cruz and Kern Counties.

		Daily		Weekly		8-wk
Site	n days	Maximum 24-hr	95th percentile 24-hr	Maximum weekly mean	95th percentile weekly mean	Mean of weekly means
Monterey/Santa Cruz Counties (8 monitoring weeks, Sept-Oct 2000)						
		ppb				
CHU	31	2.41	2.26	1.61	1.63	0.644
LJE	30	24.0	18.5	10.5	11.1	3.79
OAS	31	1.84	1.21	1.01	0.918	0.387
PMS	31	30.8	30.2	15.5	17.1	7.68
SAL	31	7.91	6.17	3.01	3.14	1.29
SES	31	16.4	12.2	8.30	7.45	2.60
Kern County (7 monitoring weeks, July-Aug 2000)						
		ppb				
ARB	25	0.996	0.556	0.507	0.507	0.189
CRS	24	14.2	25.4	4.59	5.54	2.16
MET	26	0.224	0.239	0.145	0.163	0.084
MVS	26	0.487	0.262	0.201	0.195	0.092
SHA	26	3.52	3.98	1.77	2.05	0.792
VSD	26	0.347	0.292	0.175	0.181	0.099

Exposure appraisal

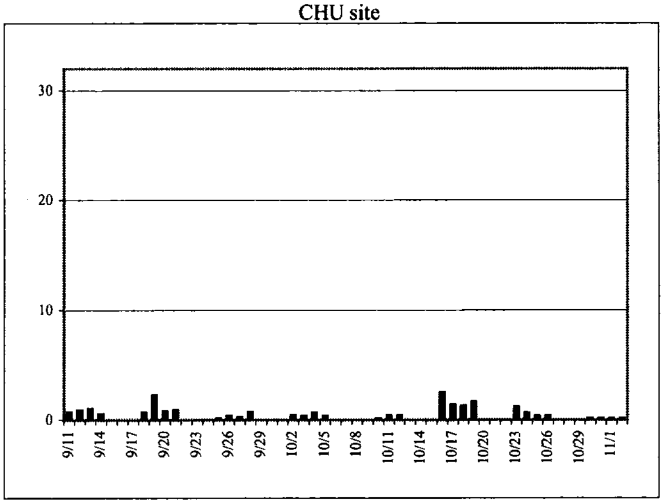
The average concentrations presented here are based on limited monitoring data and must be considered as having some degree of uncertainty. Each site is a single geographic point, monitored only 3-4 days per week for a relatively short period. The representativeness of the monitored locations and times is unknown. Further, the timing and location of nearby methyl bromide applications will influence the concentrations, and they are not yet known for the monitoring period.

cc: Tom Thongsinthusak
Lori Lim
Randy Segawa

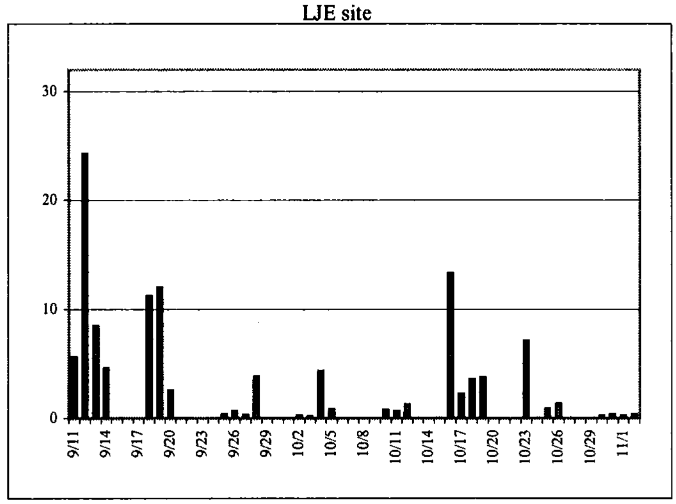
Attachments

24-hr methyl bromide concentrations (ppb) by monitoring date in Monterey/Santa Cruz Counties, Fall 2000

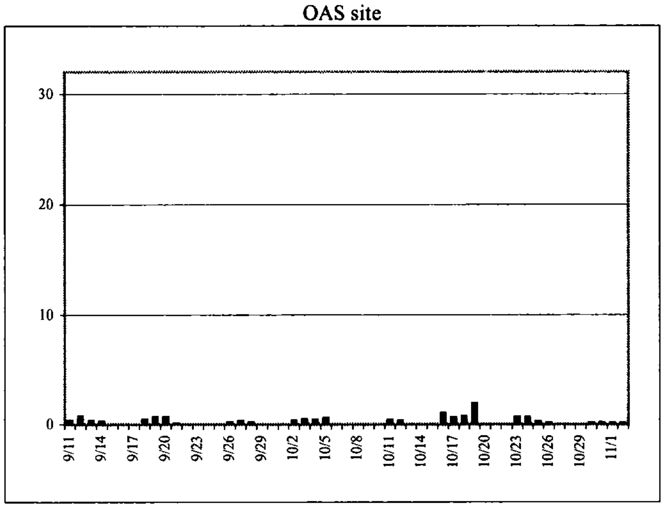
CHU site



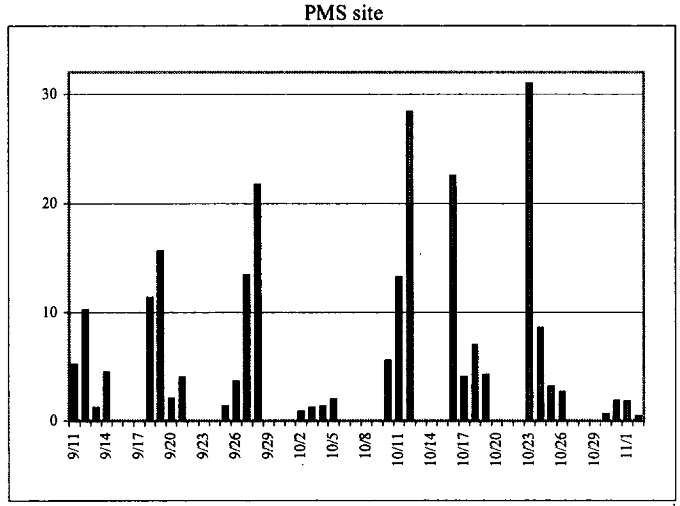
LJE site



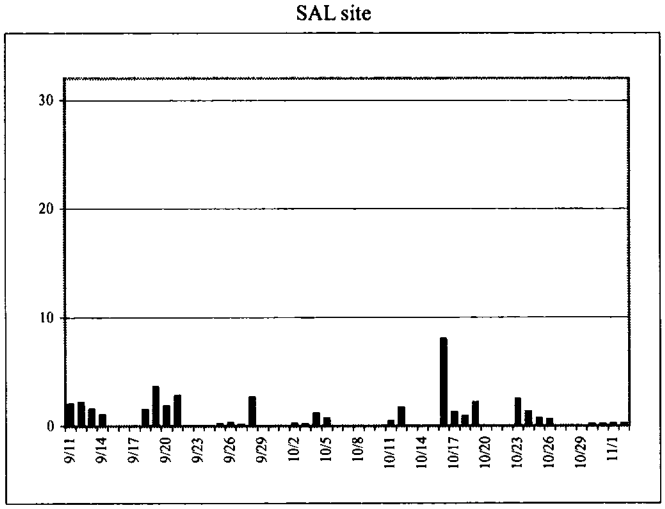
OAS site



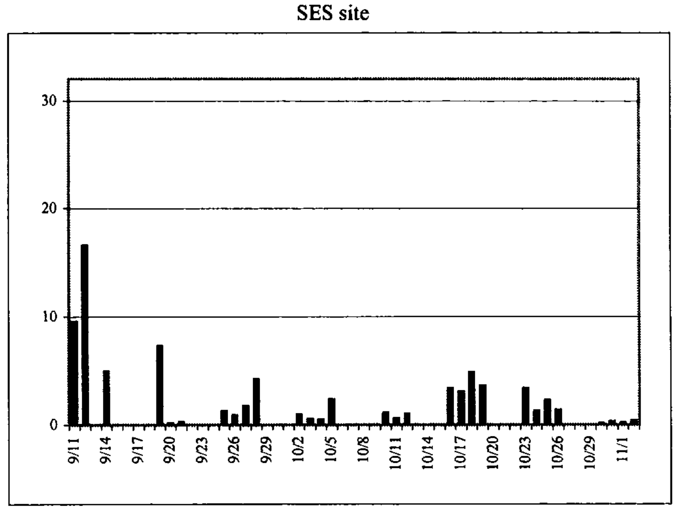
PMS site



SAL site

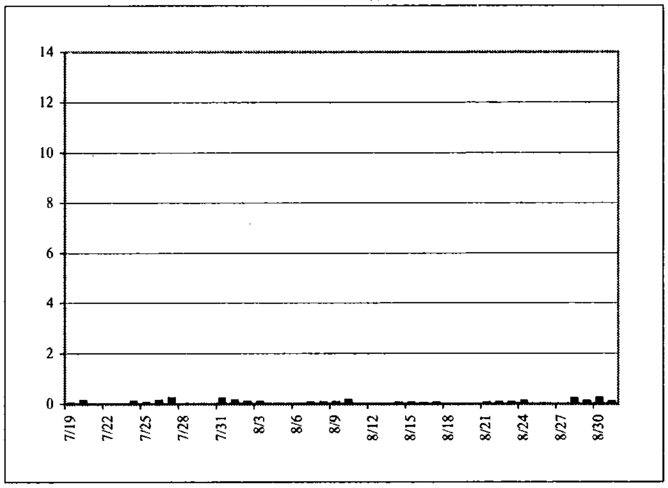


SES site

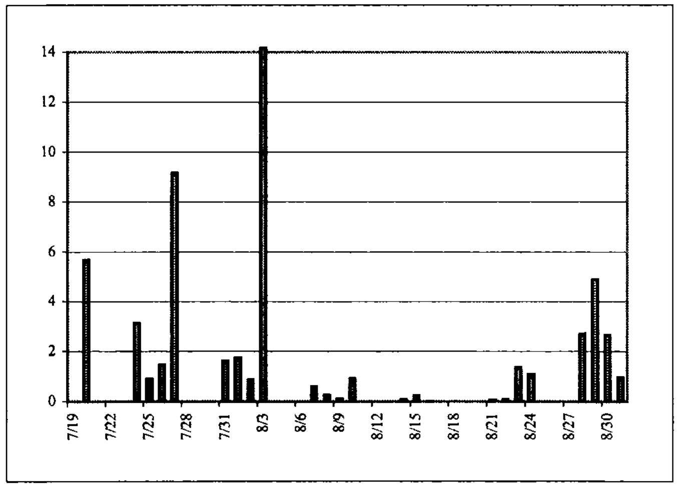


24-hr methyl bromide concentrations (ppb) by monitoring date in Kern County, Summer 2000

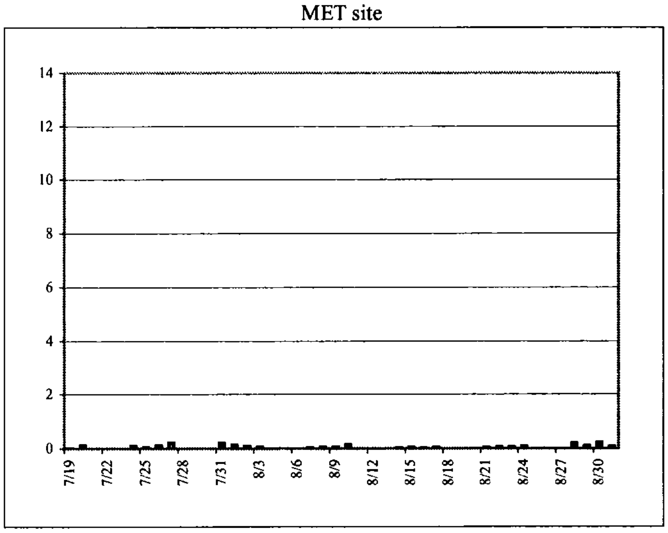
ARB site



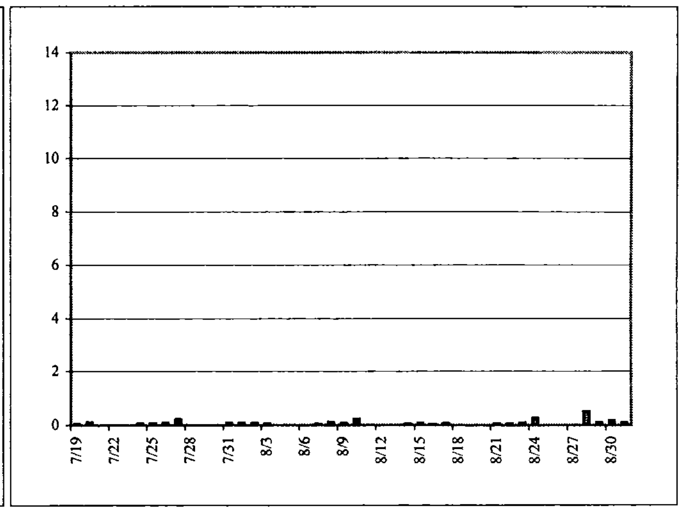
CRS site



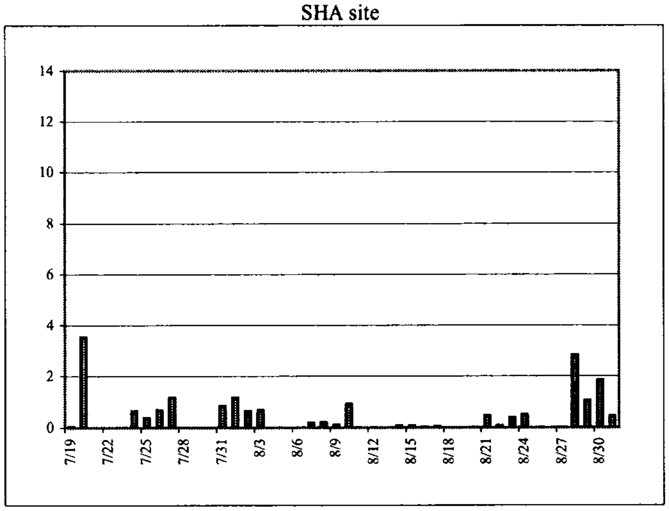
MET site



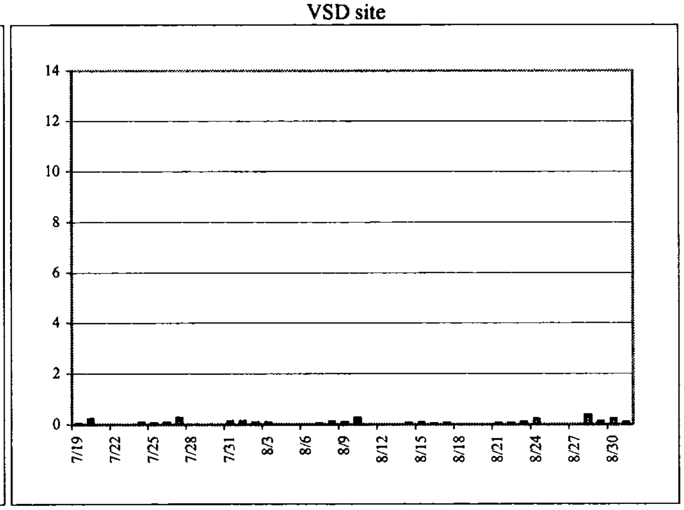
MVS site



SHA site



VSD site



Appendix C

Empirical Relationship Between Use, Area, and Ambient Air Concentration of Methyl Bromide for Subchronic Exposure Concerns

Empirical Relationship Between Use, Area, and Ambient Air Concentration of Methyl Bromide for Subchornic Exposure Concerns
Executive Summary

Background

The Department of Pesticide Regulation (DPR) has completed an initial analysis of the methyl bromide monitoring data conducted in 2000 in Kern, Monterey, and Santa Cruz counties and available methyl bromide soil use data in geographical areas in proximity to the study monitoring locations. The analysis utilized pesticide use report records collected on an accelerated basis in order to provide a timely evaluation. Other sources of information were not available under the time constraints necessary to evaluate the sources of the monitored air concentrations and prepare a mitigation strategy before the 2001 peak use season.

In order to determine the extent of methyl bromide soil applications contribution to monitored air concentrations, DPR utilized a statistical regression analysis. This was used to measure the strength of the relationship (correlation, r), to determine the extent that the methyl bromide soil use data statistically explains the air monitoring data (determination, R^2), and to establish a statistical model that characterizes the relationship. The analysis characterizes methyl bromide use by section and evaluates proximity to each monitoring station by incrementally including additional sections in a symmetrical expansion from the one that includes the location of the monitoring site.

Results

Methyl bromide soil use in sections and the monitored air concentrations were significantly correlated, with few exceptions. Methyl bromide use characterized by section areas was most consistent in explaining the air monitoring data with all 21 of 21 models establishing a significant predictive relationship. This held true for monitoring periods of 1, 4 and 7-8 weeks when analyzed with the corresponding periods of methyl bromide soil use. The best predictive models were from the 7-8 week air monitoring period, inclusive of the whole study duration. These models indicate that the methyl bromide area soil uses explains 67 to 82% of the corresponding air monitoring, statistically speaking, with the best model being the 7 x 7 section area model. This model, explaining 82% of monitored air concentrations from methyl bromide soil uses in a 7 x 7 section area, leaves only an estimated 18% left to contributing factors like weather, topography, or directional use patterns.

The best model, statistically speaking (7 x7 area methyl bromide use for 7-8 weeks), provides a means to calculate resultant air concentrations from incremental methyl bromide soil use in an area slightly larger than a township. This may be useful when evaluating mitigation strategies. Smaller area use models offer the same opportunity, with small decreases in fit, since they are all statistically significant at acceptable levels of probability (≤ 0.05).

This report employed a straight forward statistical analysis to interpret its results. Further analyses using more sophisticated statistics should be beneficial and may explain some of the anomalies visible in portions of the analyses.

Empirical relationship between use, area, and ambient air concentration of methyl bromide for subchronic exposure concerns

LinYing Li
Associate Environmental Research Scientist
Department of Pesticide Regulation
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1. Introduction

The Department of Pesticide Regulation (DPR) recommended monitoring sites and periods for air sampling to the Air Resources Board (ARB) for monitoring ambient air concentrations of methyl bromide in Monterey/Santa Cruz and Kern Counties under the Toxic Air Contamination Program (AB1807) in year 2000 [1]. These recommendations specified areas of historically heavy use areas and times of peak use in these regions. The ARB conducted air sampling and lab analysis for six sites in Monterey/Santa Cruz counties and six sites in Kern County [2,3]. The results indicated that methyl bromide air concentrations in Monterey/Santa Cruz counties were generally higher than those in Kern County. The highest 24-hour concentration observed in Monterey/Santa Cruz was 28.28 ppb, well below the 1-day acute reference levels established by the Medical Toxicology Branch of DPR (210 ppb and 250 ppb for adults and children respectively [4]). However, the 8-week average concentrations at some sites exceeded the reference level of subchronic exposure (6 to 8 weeks time frame). The reference level of human subchronic exposure are 2ppb for adults and 1ppb for children[4]. The highest 8 week average concentration was 7.73 ppb, exceeding the 1 ppb reference level.

Methyl bromide use pattern (application amount, frequency and density) near the monitoring site during the sampling period was perhaps the dominant factor that influenced air concentrations. This statistical analysis relates the measured air concentrations to the local methyl bromide use in various areas with the monitoring site as a centroid. The objectives are 1) to establish empirical relationships between air concentration and zone use of methyl bromide; 2) to estimate the size of area surrounding a monitoring site where methyl bromide applications significantly affected the air concentrations; and 3) to provide the mechanism to estimate subchronic air concentrations as a function of use. This report documents the procedure and preliminary results of using statistical methods to analyze AB1807 methyl Bromide data for year 2000. It provides the scientific basis for developing mitigation measures to reduce subchronic exposure, but the discussion of mitigation options will be described in a separate document.

2. Methods and Materials

2.1 Location of Monitoring Sites

Six sampling sites were selected in Monterey/Santa Cruz Counties, and six in Kern County. For each monitoring site, ARB provided three references for its location: 1) GPS coordinates, 2) section/township/range (STR), and 3) street numbers of the institution (usually a school) where the monitoring station was sited. Among them the section/township/range of monitoring sites is of the most interest to this analysis, because pesticide applications are referenced by Meridian Township Range Section (MTRS) in Pesticide Use Report (PUR). To make sure the MTRS is correct for each monitoring site, ArcView GIS was used to locate monitoring sites on the map. The three references did not always point to the same site on the map, although the difference was usually within one mile range. When inconsistence occurred, other tools such as Yahoo! Map were also used to assist locating of sampling sites. In the situation that all these efforts could not resolve the difference, phone calls were made to people who work in the institution where the monitoring site was located to determine its location.

The location of most monitoring sites in ARB reports was accurate enough for this analysis. However, the STR location for CHU from ARB reports was S.3/T.16S/R.3E, which was far off the site. After careful verification, it was concluded that the correct location for CHU should be S.3/T.16S/R.4E.

The final locations are listed in Table 1, and are also illustrated on Fig 1, Fig 2 and Fig 3, represented by dots on maps.

Table 1: Location of monitoring sites

County	Site	Section Township Range (STR)
Kern	ARB	S.34/T.29S/R.27E
Kern	CRS	S.33/T.27S/R.25E
Kern	MET	S.1/T.11N./R.20W
Kern	MVS	S.30/T.30S/R.28E
Kern	SHA	S.10/T.27S/R.25E
Kern	VSD	S.19/T.31S/R.29E
Mont	CHU	S.3/T.16S/R.4E
Mont	LJE	S.10/T.13S/R.3E
Mont	OAS	S.31/T.18S/R.7E
Mont	SAL	S.27/T.14S/R.3E
Santa	PMS	S.9/T.12S/R.2E
Santa	SES	S.22/T.11S/R.2E

2.2 Air Concentration

In Kern County, air sampling started on July 19th and ended on August 31st, lasting 7 weeks, while sampling in Monterey/Santa Cruz started from September 11th and ended on November 2nd, lasting about 8 weeks. The ARB provided daily average air concentration data in its summary reports [2,3] for this monitoring project. In general, the air sampling was conducted from Monday through Thursday. One exception was the first week in Kern

County, with monitoring only on Wednesday and Thursday. The average air concentration over various time periods was calculated from the daily average air concentration data for each monitoring site. It was assumed that the 4-day average could represent the average air concentration for the week.

2.3 Methyl bromide Use

Methyl bromide use surrounding the monitoring site was quantified in two ways: in an area, and in a tract (Fig.4). For example, in an area of 5X5 mile^2 centered on a section containing a monitoring site, methyl bromide use in pounds could be summed over each week. Methyl bromide use amount can also be calculated over a tract that is approximately 3 miles away (tract 3) from the monitoring site. The areas considered in this analysis range from 3X3, 5X5, ..., 15X15, and the tracts from tract 1, tract 2, ..., to tract 7. As a township covers 6X6 mile^2, areas and tracts defined above might consist of sections from more than one township. Each of included sections must be referenced with a township/meridian range/section code, in order to query the PUR table to obtain methyl bromide applications in the included section by date. On the diagram the numbers inside the township are section numbers. A Perl program (township.pl) was developed to generate MTRSs for sections in an area (Appendix 1). Township.pl takes a station's STR as shown in Table 1, and prints on the screen or to a file a matrix of MTRSs for the square block of surrounding sections depending on the specified size.

Three township and range reference coordinate systems are used in California: the Mount Diablo, San Bernardino and Humboldt, with the Mount Diablo system covering the biggest area. All of the sampling sites are located in the Mount Diablo system [5]. However, one monitoring site in Kern County (MET) was very close to the boundary between the Mount Diablo system and the San Bernardino system. Areas and tracts included sections in both systems. The program can not handle this situation yet. In addition, the size and arrangement of sections at this boundary is not confined to 1 square mile section configuration used elsewhere. Therefore, this site was dropped from the analysis.

The emission of methyl bromide from soil could last up to several days, or could largely occur in the first 48 hours, depending on the application methods, soil status and meteorological conditions. Air sampling was taken from Monday through Thursday. Therefore, the use week relevant to a weekly average concentration was defined from Friday of the previous week to Thursday of the current monitoring week. The weekly zone use of methyl bromide over various areas was calculated with a perl program (mb_use01.pl), which is appended in this document (Appendix II).

2.4 Methods to relate the air concentration to the methyl bromide use

According to the Gaussian equation, air concentration is proportional to the flux rate under fixed soil status and weather conditions. When considering a large area and over a long period, this linear proportionality can be extended to the relationship between air concentration and the amount of methyl bromide used in the area. The Linear Regression Model was used to relate the air concentration to the methyl bromide use:

$$Y = a + bX \tag{1}$$

where Y is the average air concentration over a certain period (1 week, 3 to 4 weeks and 7 to 8 weeks), and X is the weekly average methyl bromide use over various areas or tracts in that period.

R^2 and Error Mean Square(EMS) measure the fitness of the Linear Regression Model. R^2 represents the percentage of variation of the dependent variable that is explained by the independent variable, and it is often referred to as the coefficient of determination. EMS is the average squared residuals (errors) not being explained by the model, which is defined as:

$$EMS = \sum_{i=1}^{n} \frac{(Y_i - \hat{Y}_i)^2}{n-2} \tag{2}$$

where n is the number of samples, Y_i and $\hat{Y}_i$ are measured and calculated air concentrations, respectively. The higher R^2 and lower EMS means better regression.

The least squares method was used to estimate regression coefficients a and b. Confidence intervals for a, b and R^2 were calculated using methods described in [6]. A computer program (linear.pl) was developed to conduct regression analysis (Appendix III).

If the regression analysis yields useful relationships, then given an air concentration C, the corresponding use, represented in the X variable, can be solved for by using the equation below:

$$X = (C - a)/b \tag{3}$$

The use X is in lb/week over certain areas (3x3, 5x5, ..., 15x15), and C, the concentration, is in ppb.

3. Results

3.1 Air concentration

Weekly average air concentrations (ppb) in various sites was listed in Table 2. Based on weekly average concentrations, air concentrations over a longer period such as 3 or 4 weeks and 7 or 8 weeks was also calculated (Table 3).

The air concentration of methyl bromide changed from site to site and from week to week over the monitoring periods (Fig. 5). The highest concentration (15.58 ppb) was observed at PMS in Santa Cruz County in week 5. In fact, the air concentration at PMS was consistently higher than other Monterrey stations except in week 1. In Kern County, CRS had higher concentration than other sites except in week 1. Moreover, air concentrations in all places appeared to be lower in some weeks, and higher in other weeks. For example, during weeks 4, 5 and 6, all sites in Kern County reported low air concentrations, while for Monterey/Santa Cruz Counties, low concentrations occurred in weeks 4 and 8.

Table 2: Weekly average air concentrations (ppb)

County	Site	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8
Kern	ARB	0.507	0.132	0.292	0.111	0.039	0.059	0.188	
Kern	CRS	2.828	3.647	4.595	0.459	0.150	0.641	2.790	
Kern	MET	0.064	0.111	0.115	0.070	0.030	0.059	0.145	
Kern	MVS	0.061	0.095	0.066	0.096	0.034	0.092	0.201	
Kern	SHA	1.775	0.705	0.815	0.332	0.043	0.347	1.536	
Kern	VSD	0.112	0.099	0.091	0.104	0.033	0.081	0.175	
Monterey	CHU	0.730	1.300	0.340	0.400	0.260	1.610	0.590	0.110
Monterey	LJE	10.630	8.470	1.270	1.350	0.830	5.630	2.580	0.250
Monterey	OAS	0.380	0.440	0.170	0.400	0.250	1.010	0.390	0.080
Monterey	SAL	1.640	2.360	0.770	0.500	0.700	3.010	1.200	0.140
Santa Cruz	PMS	5.170	8.140	9.890	1.270	15.580	9.490	11.210	1.110
Santa Cruz	SES	8.340	2.880	1.960	1.020	0.840	3.630	2.010	0.220

Note: The 1-week NOEL reference concentrations for adult and children are 120 ppb and 70 ppb respectively [4].

Table 3: Average air concentrations(ppb) over 3/4 weeks and 7/8 weeks

County	Site	Average air concentration (ppm)		
		1st 4-weeks	2nd 4-weeks or 3-weeks	7/8-weeks
Kern	ARB	0.261	0.095	0.19
Kern	CRS	2.882	1.194	2.16
Kern	MET	0.090	0.078	0.08
Kern	MVS	0.080	0.109	0.09
Kern	SHA	0.907	0.642	0.79
Kern	VSD	0.102	0.096	0.10
Monterey	CHU	0.693	0.643	0.67
Monterey	LJE	5.430	2.323	3.88
Monterey	OAS	0.348	0.433	0.39
Monterey	SAL	1.318	1.263	1.29
Santa Cruz	PMS	6.118	9.348	7.73
Santa Cruz	SES	3.550	1.675	2.61

Note: The 6-week NOEL reference concentrations for adult and children are 2 ppb and 1 ppb respectively [4].

Many factors might have contributed to these highs and lows, such as weather conditions, methyl bromide use patterns, and topographical characteristics near the monitoring sites. In Figures 6 and 7, the weekly air concentration was compared to the weekly methyl bromide use in an area of 13x13. In Kern County, low methyl bromide use corresponded to low concentration except in week 5 at SHA and CRS (Fig. 7). These two sites with higher concentrations (SHA and CRS) were located in the same township, and were close to each other. The methyl bromide use calculated from the PUR report was exactly the same for both sites. However, the air concentrations differed between these two sites, indicating the use data alone could not completely explain the variation of air concentration. The data of Monterey/Santa Cruz Counties also show a linear tendency between air concentration and the amount of use, but failed to explain every single data point.

3.2 Effect of Temporal Scales

In the regression model (1), air concentration and methyl bromide use can be calculated over various periods. By examining R^2 and EMS values, we can determine over what period the methyl bromide use is closely related to the air concentration.

Table 4: R^2 between average air concentration (ppb) and average methyl bromide usage (lb/week) over various areas, tracts and periods

Area/Tract	**Time period over which the average value was calculated**					
	1 week (n = 83)		**4 weeks (n = 22)**		**7/8 weeks (n = 11)**	
	R^2	EMS	R^2	EMS	R^2	EMS
area 3x3	0.489	4.79	0.615	2.29	0.727	1.61
area 5x5	0.346	6.25	0.464	3.19	0.669	1.96
area 7x7	0.457	5.19	0.584	2.47	0.821	1.06
area 9x9	0.454	5.21	0.562	2.60	0.769	1.37
area 11x11	0.463	5.13	0.621	2.25	0.779	1.31
area 13x13	0.427	5.48	0.581	2.49	0.703	1.75
area 15x15	0.419	5.55	0.570	2.55	0.675	1.92
tract 1	0.498	4.79	0.615	2.29	0.727	1.61
tract 2	0.138	8.24	0.246	4.48	0.459	3.20
tract 3	0.415	5.59	0.623	2.24	0.846	0.91
tract 4	0.209	7.55	0.307	4.12	0.381	3.66
tract 5	0.191	7.73	0.406	3.53	0.403	3.53
tract 6	0.043	9.14	0.093	5.39	0.068	5.51

tract 7	0.003	8.66	0.167	4.95	0.158	4.98
Significant R values						
$R_{0.05}$	0.215		0.413		0.576	
$R_{0.01}$	0.280		0.526		0.708	

Note: R^2 is often referred as the coefficient of determination, representing the percentage of variation of air concentration that is explained by the use of methyl bromide. EMS is the average squared residuals (errors) not being explained by the model.

Table 4 shows correlations between average air concentration and methyl bromide use in various areas and tracts and over various periods. The correlation coefficient between air concentration and methyl bromide use is significant over many areas and time periods (Table 4). R^2 values are higher over longer periods. However, the significant R-value threshold also increases when the number of samples decreases. For most areas and tracts, the EMS declined with longer periods. The regression model using 7 to 8-week average data generated the least EMS. More noises in the concentration-methyl bromide use relationship were filtered out when the averaging period gets longer.

Because the 7 to 8-week averaging period yielded the highest correlation and the lowest EMS values, and because the main concern of this study is subchronic effects which typically results from 6-8 weeks' exposure, analyses in following paragraphs will be based on the 7 to 8-week average data.

3.3 Effect of spatial scales

Dispersion of methyl Bromide may reach several miles away from the application sites. However, methyl bromide use in a certain area around the monitoring sites might have the better correlation to the air concentration. The methyl bromide uses in various areas and tracts around each monitoring site, along with the air concentration are shown in Figures 8 and 9. The methyl bromide use increased when the area was expanded. The air concentration agreed well with the methyl bromide use amount in both low and high ends. The correlation between air concentration and use over the area of 7X7 shows the better results (Table 4). The relationship between the air concentration and the methyl bromide use in a tract is obscure, suggesting that the application of methyl bromide to a particular tract alone does not explain very well the variation of air concentration. Nevertheless, tract 3 had the highest determination coefficient ($R^2 = 0.846$, Table 4).

Linear regression between the air concentration and methyl bromide use was conducted over various areas (Figures 10 and 11). In the linear model (1), Y is air concentration (ppb), and X is the methyl bromide use in an area (lb/week). Regression coefficients a and b have a clear meaning: a represents the air concentration when there is no methyl bromide use in the considered area, and b represents the increase of air concentration resulting from one unit increased methyl bromide use. The coefficient 'a' can also be interpreted as the background concentration for that given area. In this analysis,'a' was always a positive number, which means there was net methyl bromide drifting into the area from other places (Table 5). The smaller the area, the bigger the 'a' value, implying that air concentration in a smaller area received more contribution from outside areas. The a-value is close to zero after the area is bigger than 9X9 (Fig. 12), indicating at this size the inflow is balanced by the outflow.

The coefficient b decreases exponentially when the area increases (Fig. 12). When the area is bigger, one unit methyl bromide use has less effect on the air concentration. To compare b values calculated from different areas, b must be normalized by its area, this will give the degree of impact of unit use on unit area. The normalized b value was obtained by multiplying b with the area. It represents the concentration increase induced by one unit use (lb/week/section) in all sections contained in that area. Because of the boundary effects, 1lb/week/section use in a small area does not cause air concentration increase as much as it does over a large area.

The data fitting effect by the linear regression is indicated by R^2 and EMS. Although R^2 and EMS vary with the size of area, no apparent tendency is observed. The best fitting is obtained from use data over the area of 7x7 (Table 5).

Table 5: regression coefficients, correlation coefficient and normalized values of regression coefficient b

area	a	b	normalized b	R^2	EMS
3x3	0.8765	0.000456	0.0041	0.727	1.61
5x5	0.5281	0.000224	0.0056	0.669	1.96
7x7	0.2245	0.000138	0.0068	0.821	1.06
9x9	0.1925	0.000097	0.0079	0.769	1.37
11x11	0.0767	0.000079	0.0096	0.779	1.31
13x13	0.0381	0.000066	0.0112	0.703	1.75
15x15	0.0632	0.000060	0.0135	0.675	1.92

Although the regression coefficients and correlation coefficient differ with the size of areas, statistically the differences are not significant. The 95%confidence intervals(CI) of these coefficients do overlap with each other (Table 6). In fact, all of the 95% confidence intervals for coefficient a contain 0, indicating that 'a' is not significantly different

Table 6: 95% confidence Intervals for a, b and R^2

Area	a			b			R^2		
	estimate	CI_1	CI_2	estimate	CI_1	CI_2	estimate	CI_1	CI_2
3x3	0.876	-0.090	1.844	0.00046	0.00025	0.00067	0.73	0.27	0.92
5x5	0.528	-0.643	1.700	0.00023	0.00011	0.00034	0.67	0.18	0.90
7x7	0.224	-0.672	1.122	0.00014	0.00009	0.00019	0.82	0.45	0.95
9x9	0.192	-0.847	1.233	0.00010	0.00006	0.00014	0.77	0.34	0.94
11x11	0.077	-0.969	1.123	0.00008	0.00005	0.00011	0.78	0.36	0.94

13x13	0.038	-1.213	1.291	0.00007	0.00003	0.00010	0.70	0.23	0.92
15x15	0.063	-1.250	1.378	0.00006	0.00003	0.00009	0.68	0.19	0.91

from 0. In all cases, the confidence interval is narrowest when distance is 3, corresponding to a 7X7 area. The coefficient b for smaller areas (3X3 or 5x5) is significantly different from those calculated from areas larger than 9X9.

4. Summary

This analysis examined the relationship between use, area and time period and measured air concentrations for methyl bromide. There were significant regression relationships between use and measured air concentrations for differing time periods and differing area sizes. The relationship giving the highest R^2 value and the lowest EMS value utilized 8 weeks and a 7x7 square mile area of use surrounding each monitoring site.

There are several caveats to this analysis. First, this analysis only includes pesticide use data from field fumigations. Pesticide use data for structural, commodity, and other types of methyl bromide fumigations is not amenable to this type of analysis because it does not include information on specific location or date, and is incomplete for 2000. Structural or commodity fumigations may have occurred during the monitoring, but there is no way to take their contribution to the air concentrations into account. However, these effects were probably minor, based on the strength of the statistical relationships determined in the analysis. Second, this analysis assumes that all pesticide use data for field fumigations is complete and accurate. Missing or incorrect data could significantly alter the regressions. Missing data would cause an underestimation of the amount of methyl bromide that correlates with a specific air concentration. In other words, the 1 ppb reference concentration would equate to more than 18,000 pounds per township per month if some fumigations were not reported. Incorrect data, where reported use was inflated, would cause an overestimation of the amount of methyl bromide that correlates with a specific air concentration. We think this is unlikely, however, since use rates in the analysis were within reasonable ranges. Third, the regression line represents the mean estimate of the amount of methyl bromide versus air concentration, with half the data points above the line and half below. In other words, if 18,000 pounds per township per month of methyl bromide were applied, monitoring should show half the air concentrations greater than 1 ppb, and half less than 1 ppb, all other factors being equal. Fourth, while there are significant differences in emission rates between methods over a 24-hour period, it is likely that there is little difference between methods in emissions over several weeks. Adjustments for method differences do not appear to be necessary for subchronic exposure mitigation. However, additional monitoring is needed to verify this assumption.

Acknowledgment

This study was conducted under the guidance of Randy Segawa and Bruce Johnson, Senior Environmental Research Scientists in the DPR. Bruce checked part of statistical analysis[7] and reviewed the draft of this report[8]. Craig Nordmark provided GIS maps for locating monitoring sites.

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[2] ARB, 2001. Ambient air monitoring for methyl bromide and 1,3-Dichloropropene in Monterrey/Santa Cruz Counties - Fall 2000. California Air Resources Board. Sacramento, CA.

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[4]DPR, 1999. Methyl bromide risk characterization document for inhalation exposure (Draft RCD 99-02). California Department of Pesticide Regulation, Sacramento, CA.

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[7] Johnson Bruce, May 1, 2001. Mini memo to Randy Segawa and LinYing Li: Verification of calculations involved in estimating relationship between use, use zone, and air concentrations monitored by ARB under 1807 program for methyl bromide .

[8] Johnson Bruce, May 7, 2001. A memo to LinYing Li: Review of the preliminary analysis of 1807 methyl bromide data for year 2000 (draft).

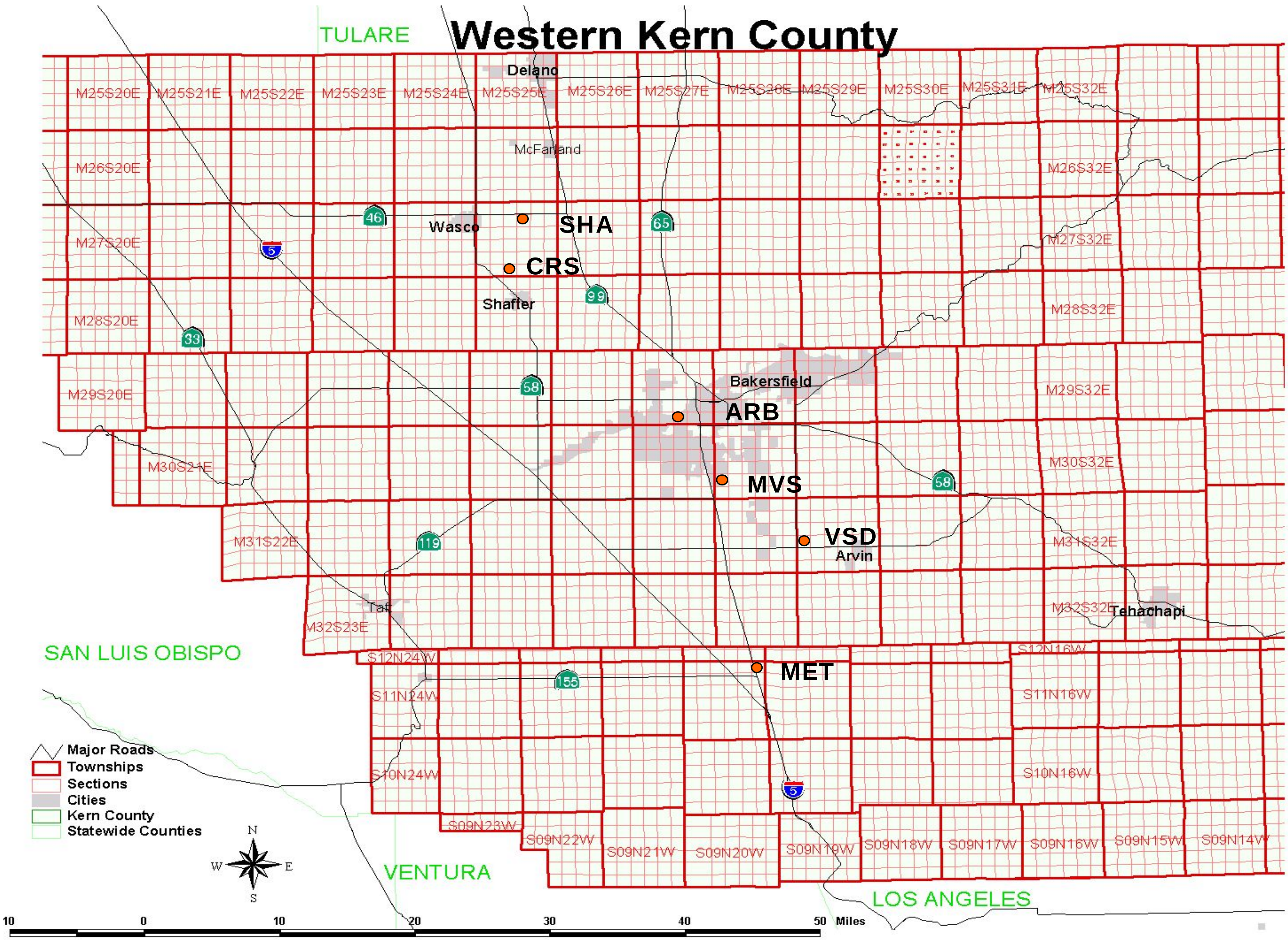


Figure 1 Monitoring sites in Kern County

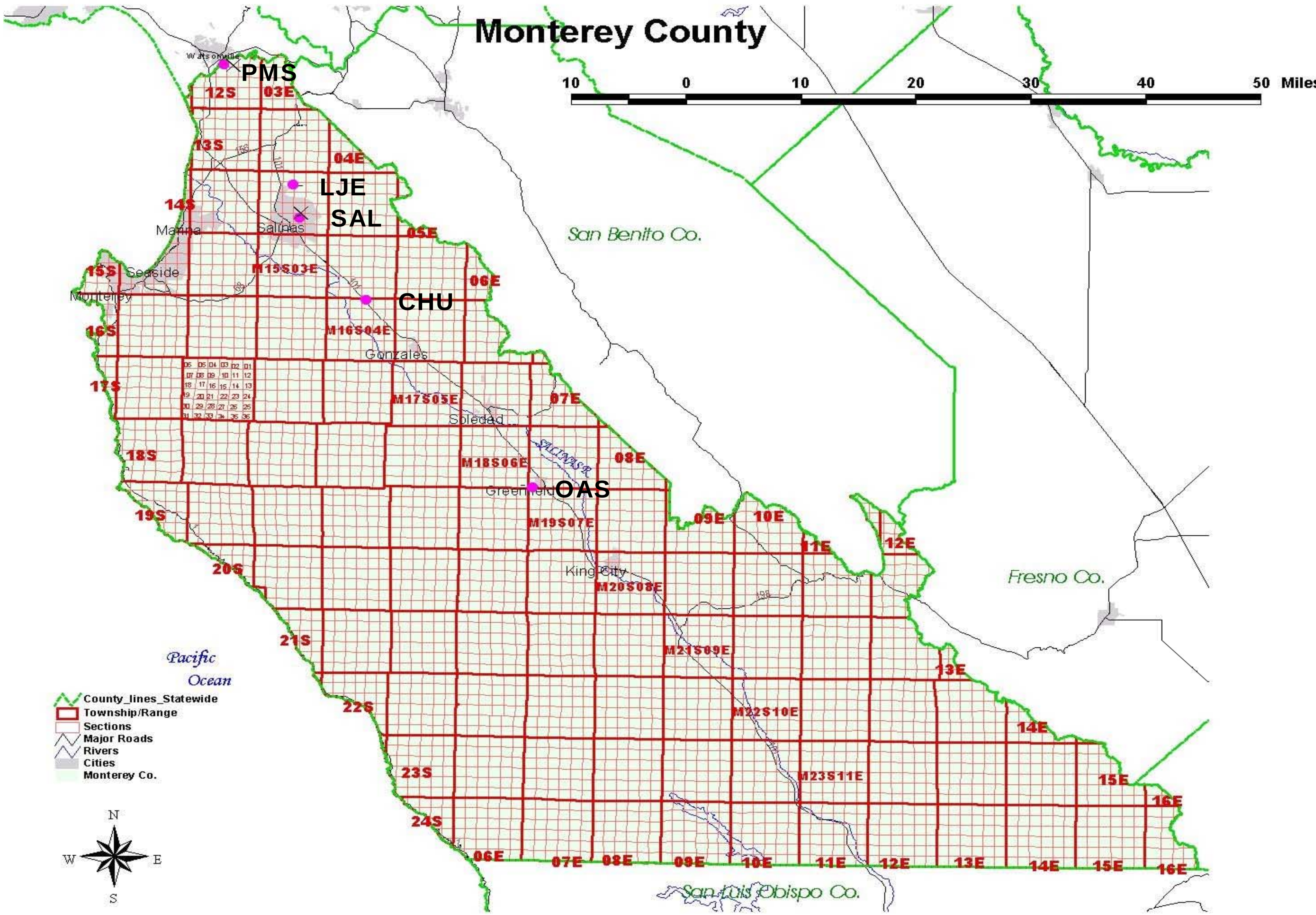


Figure 2 Monitoring sites in Monterey County

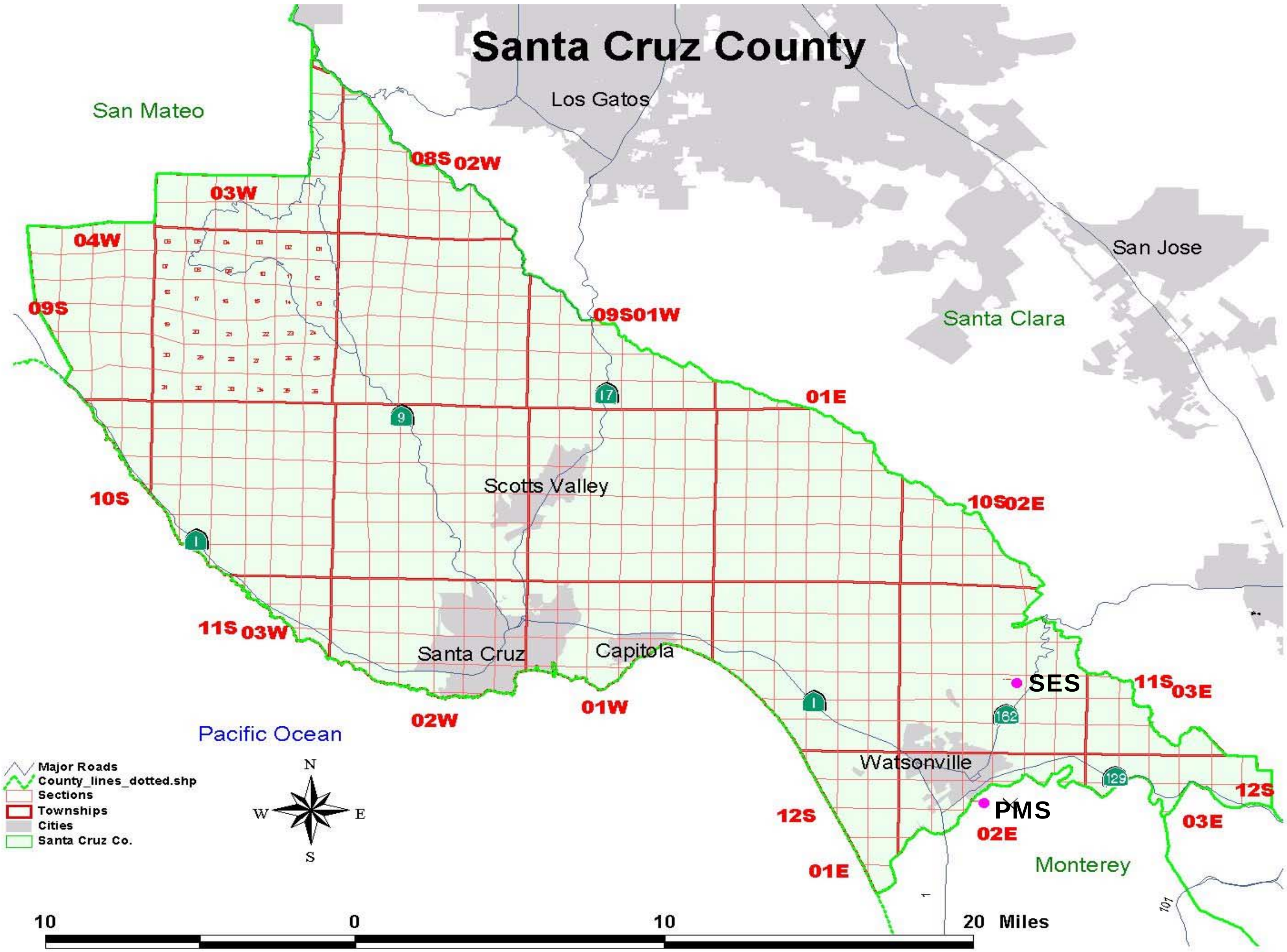


Figure 3 Monitoring sites in Santa Cruz County

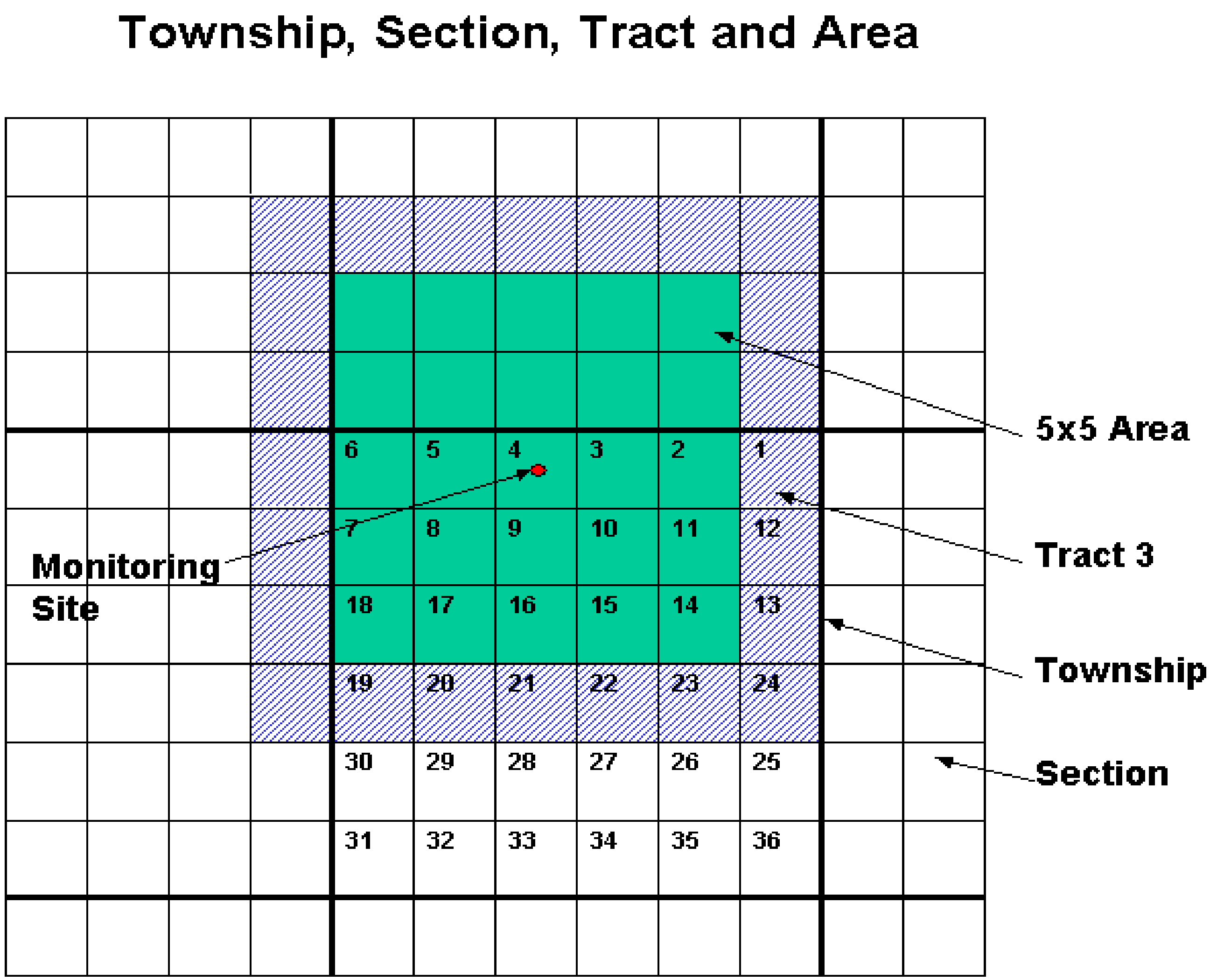


Figure 4 A diagram of township, section, area and tract in relation to the monitoring site

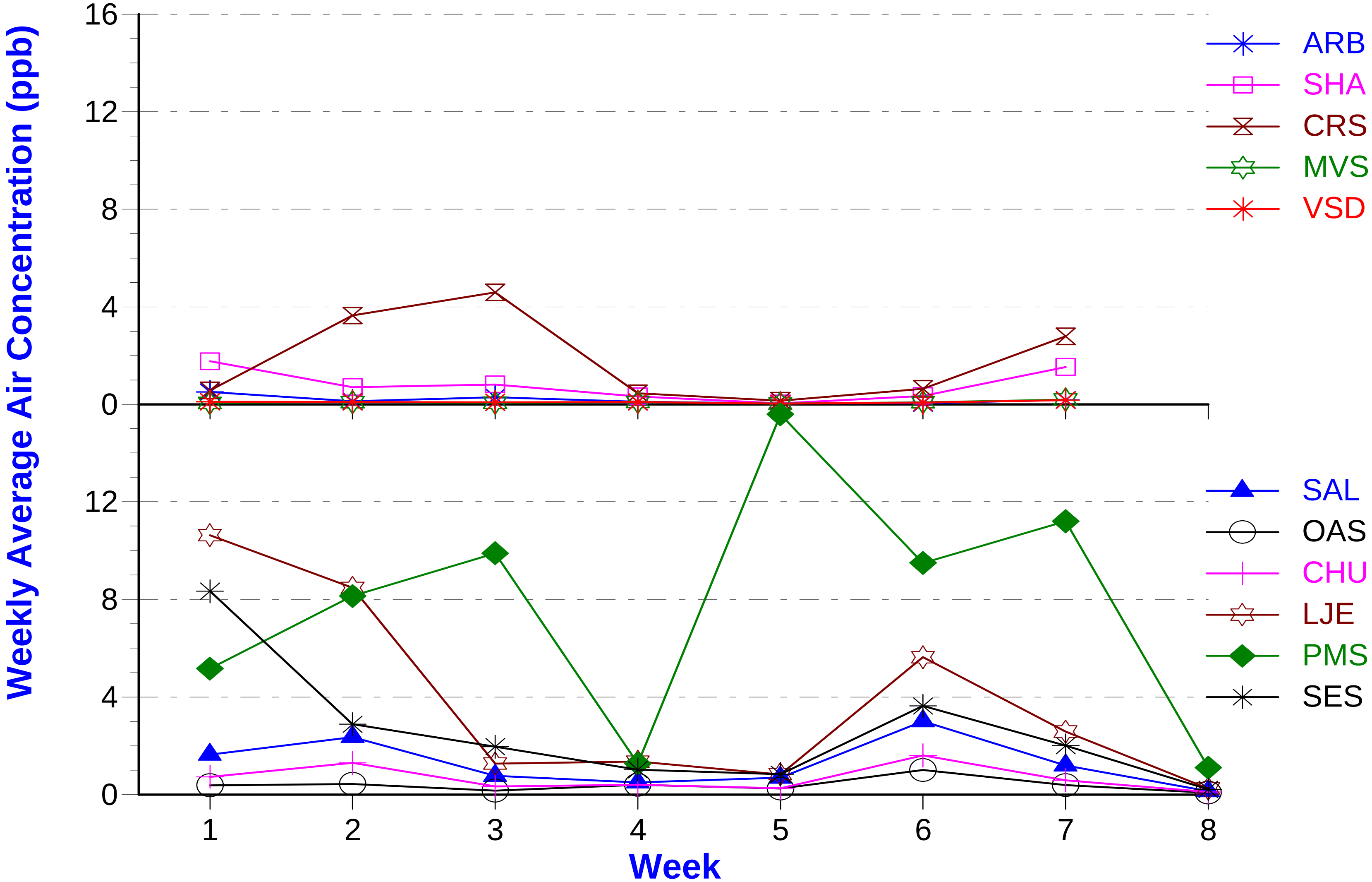


Figure 5 The variation of weekly average air concentrations at various monitoring sites

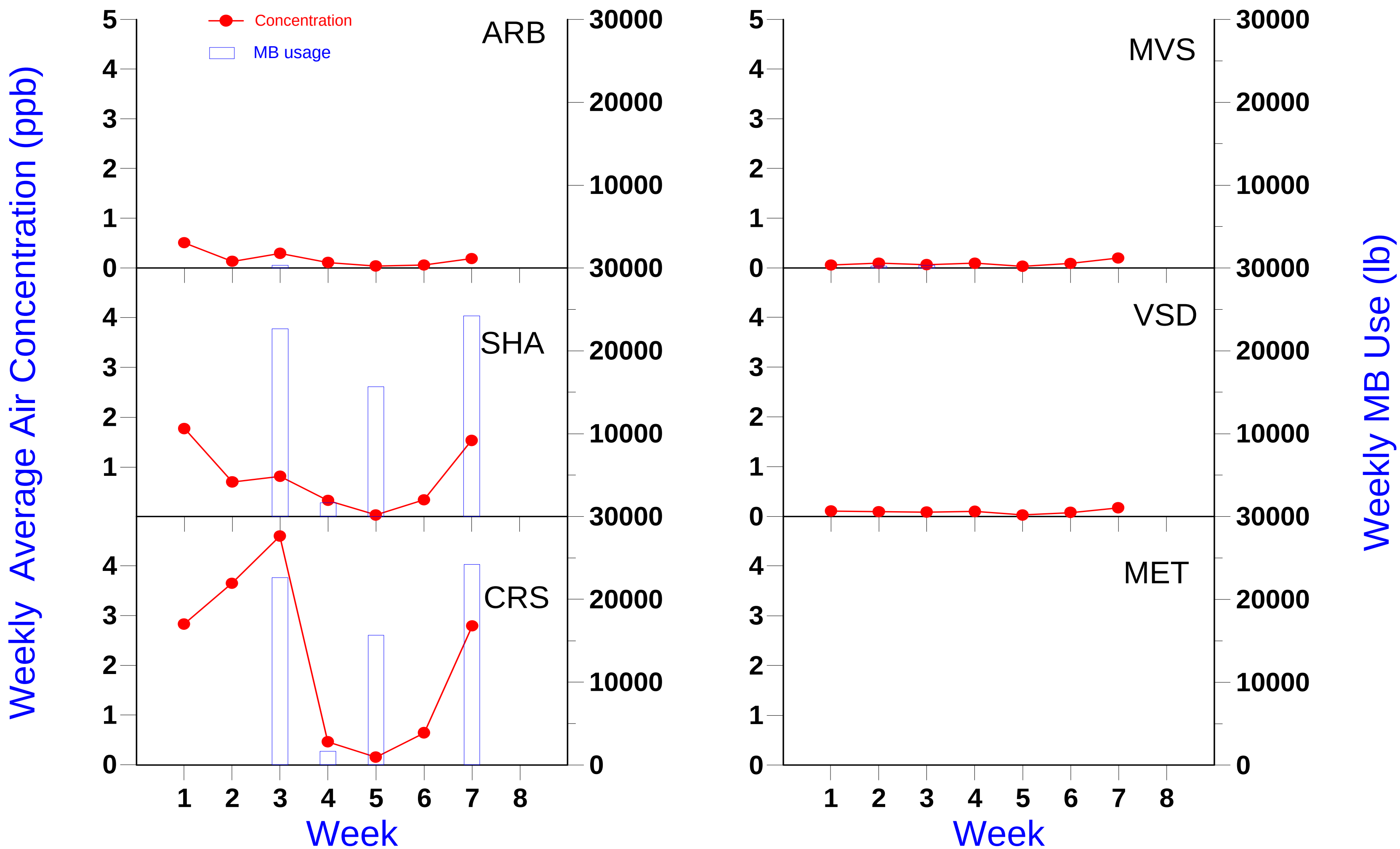


Figure 6 Weekly average air concentration and weekly MeBr use (13x13 area) in Kern County

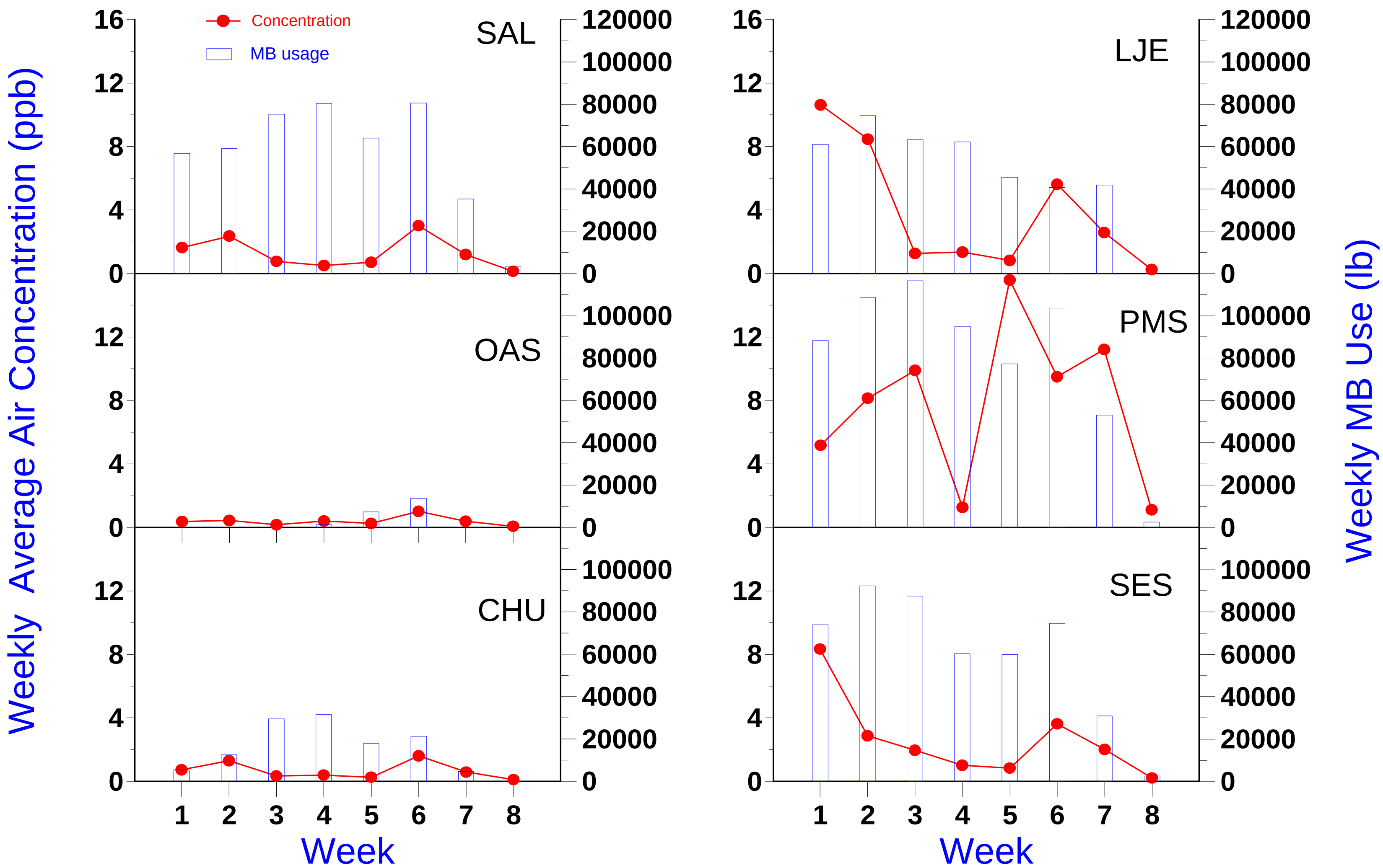


Figure 7 Weekly average air concentration and weekly MeBr use (13x13 area) in Monterey/Santa Cruz Counties

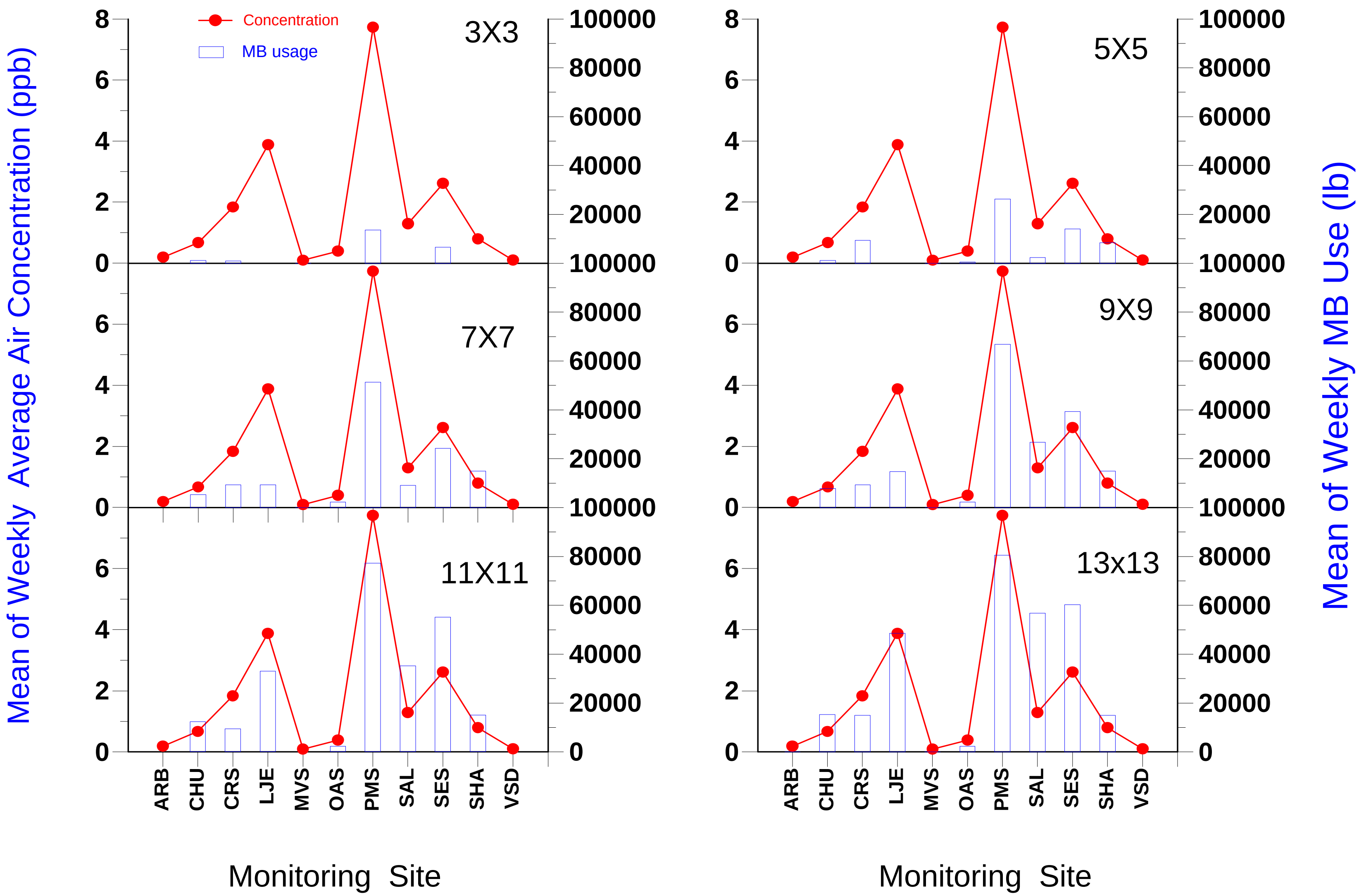


Figure 8 Mean of weekly air concentration and mean of weekly MeBr use in various areas (over 7 or 8-week period)

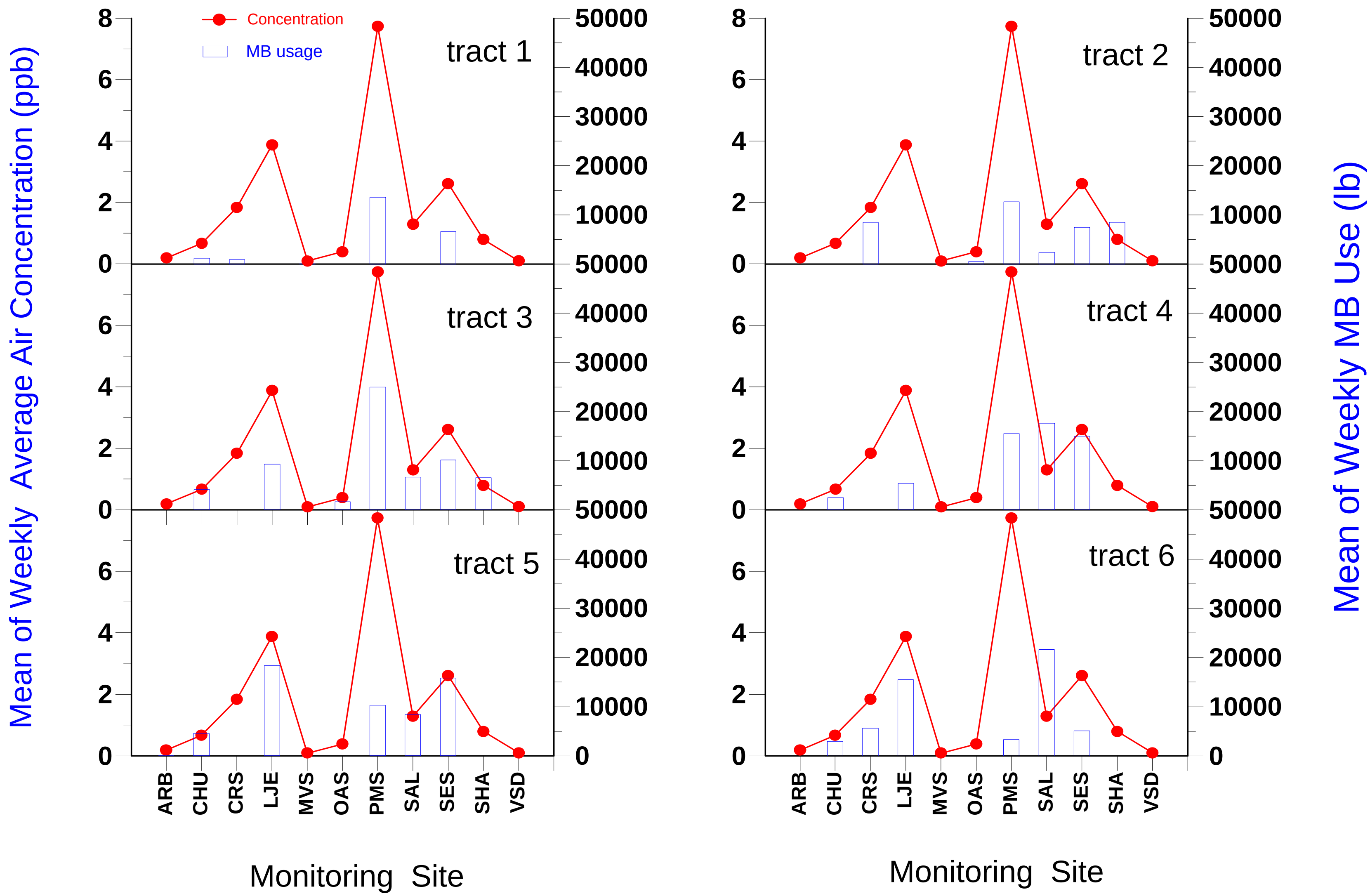


Figure 9 Mean of weekly average air concentrations and mean of weekly MeBr use in various tracts (over 7 or 8-week period)

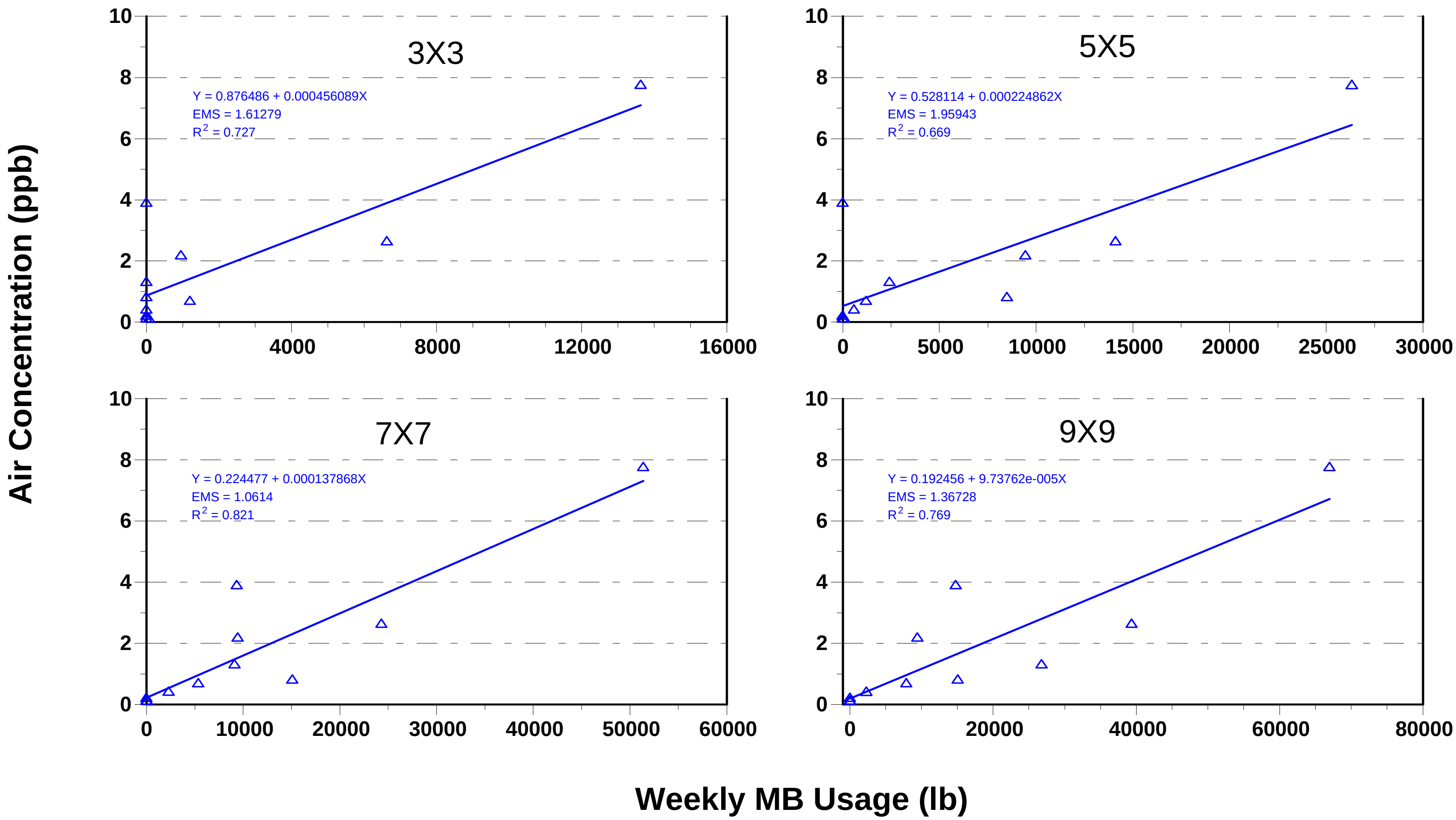


Figure 10 Regression: Mean of weekly average air concentrations vs Mean of weekly MeBr uses over various areas (over 7 or 8-week period) (a)

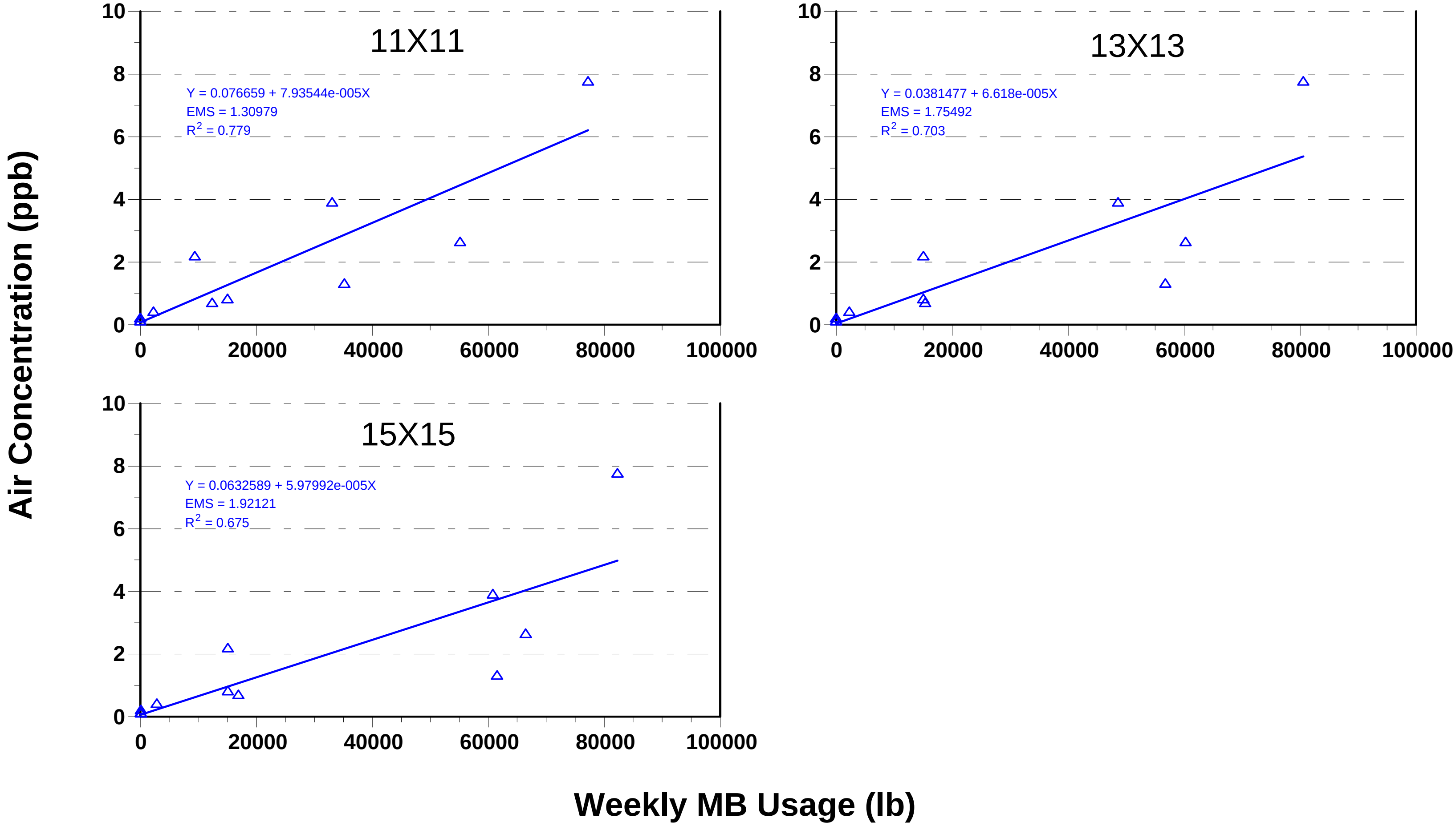


Figure 11 Regression: Mean of weekly average air concentrations vs Mean of weekly MeBr uses over various areas (over 7 or 8-week period) (b)

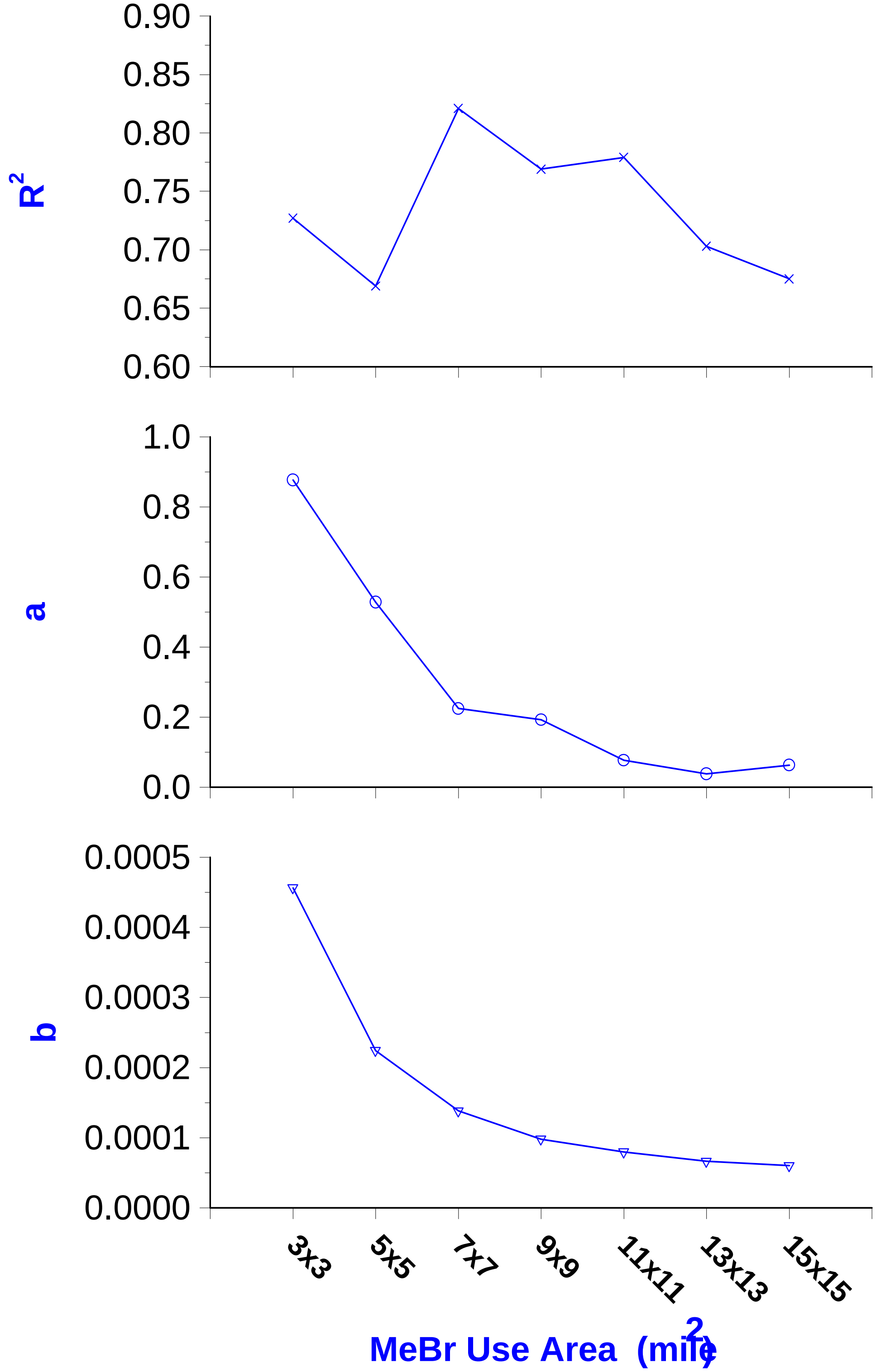


Figure 13 The variation of R^2, a and b with the size of MeBr use area

Appendix I.

A Perl program for determining the neighboring sections in the township & meridian range system

1. Important notes

- Two coordination systems separately for the township&Range, and sections
- For township&Range, must have algorithm
  - to calculate the numerical component, and
  - to determine the directional component
- For sections, must have algorithm
  - to convert from XY coordinates to section number, and
  - to convert from section number to XY coordinates
- Three systems are used in California, Boundaries issues between two systems (not solved yet)

- two types of notation: MTRS and STR, the algorithm must be able to parse and assembly the two notations
  - -The input is in STR format, which was used in ARB's reports
  - -The output is in MTRS, which was adopted in PUR reports

2. Source file (township.pl)

```
#!/usr/local/bin/perl -w
#    Last change:  LI   12 Apr 2001    9:57 am
# township.pl
# Generates strings representing the surrounding MTRS(Meridian Township Range
Section)
# for a giving MTRS within the specified distance
# -----------------------------------------------------------

# all parameters are fed from command line
# usage: township.pl MTRS DX,DY
# Please note two forms of MTRS: S.3/T.16S/R.3E or M16S03E03
# The first form was used for arb monitoring project
# The second for was used in DPR's PUR report
# This program assumes the input in the first format and generates MTRS in the
2nd format



#my ($MTRS, $DX, $DY)= @ARGV;
#print "@ARGV\n";

$working_dir = 'E:\Arb\1807';
chdir $working_dir;

sub_MTRS("S.19/T.31S/R.29E", 3,7);
```

```
# ------------------------------------------------------------ #
# usage: sub_MTRS(STR, DX, DY)
sub sub_MTRS {
my ($STR, $DX, $DY) = @_;

# extracting section number, township and range for the sampling site
$STR =~ m/S.(\d+)\/T.(\d+)([A-Z])\/R.(\d+)([A-Z])/;
$S=$1;
$T_val = $2;
$T_dir = $3;
$R_val = $4;
$R_dir = $5;
$MTRS= "M"."$T_val"."$T_dir"."$R_val"."$R_dir"."$S";
print "$STR\t $MTRS\n";
#print "$S,  $T_val,  $T_dir,  $R_val,  $R_dir\n";

# get coordinate for the sampling section
 $n = int($S/6) + 1;
 if($n==1 or $n==3 or $n==5) {
    $m = $n*6 + 1 - $S;}
 else {
    $m = $S - ($n-1)*6;}
 #print "$m, $n\n";

# calculating MTRS for surrounding grids


for ($j=-$DY; $j<=$DY; $j++){
for ($i=-$DX; $i<=$DX; $i++){
        # first, get coordinate for the surrounding sections, also the
township value and range value
        $sx =$m+$i;
        if($sx>6){
            $RR_val = $R_val + int($sx/6);
            $sx=$sx-6*int($sx/6);}
        elsif($sx<1){
             $RR_val = $R_val - (1+abs(int($sx/6)));
             $sx=$sx+6*(1+abs(int($sx/6)));}
        else {
             $RR_val = $R_val;}

        $sy =$n+$j;
        if($sy>6){
            $TT_val = $T_val + int($sy/6);
            $sy=$sy-6*int($sy/6);}
        elsif($sy<1){
             $TT_val = $T_val - (1+abs(int($sy/6)));
             $sy=$sy+6* (1+abs(int($sy/6)));}
        else {
             $TT_val = $T_val;}

        # The directions for township and range are the same with those of
sampling site
        # Need more analysis here
        $TT_dir = $T_dir;
        $RR_dir = $R_dir;

        # then, get the section number from its xy coordinates
```

```
        if($sy==1 or $sy==3 or $sy==5) {
           $SS = $sy*6 - $sx + 1;}
        else {
           $SS = ($sy-1)*6 + $sx;}

        # now, get the MTRS
        if ( $TT_val <=9 ) {$TT_val = "0"."$TT_val";}
        if ( $RR_val <=9 ) {$RR_val = "0"."$RR_val";}
        if ( $SS <=9 ) {$SS = "0"."$SS";}

        $new_MTRS = "M"."$TT_val"."$TT_dir"."$RR_val"."$RR_dir"."$SS";
        print "$new_MTRS ";

} # end of i loop
print "\n";
} # end of j loop

} # end of sub
```

3. Examples

Surrounding sections of a monitoring site (PMS 7X7)

```
Command Prompt

E:\ARB\1807>township.pl
S.9/T.12S/R.2E    M12S2E9
M11S01E25 M11S02E30 M11S02E29 M11S02E28 M11S02E27 M11S02E26 M11S02E25
M11S01E36 M11S02E31 M11S02E32 M11S02E33 M11S02E34 M11S02E35 M11S02E36
M12S01E01 M12S02E06 M12S02E05 M12S02E04 M12S02E03 M12S02E02 M12S02E01
M12S01E12 M12S02E07 M12S02E08 M12S02E09 M12S02E10 M12S02E11 M12S02E12
M12S01E13 M12S02E18 M12S02E17 M12S02E16 M12S02E15 M12S02E14 M12S02E13
M12S01E24 M12S02E19 M12S02E20 M12S02E21 M12S02E22 M12S02E23 M12S02E24
M12S01E25 M12S02E30 M12S02E29 M12S02E28 M12S02E27 M12S02E26 M12S02E25
```

Surrounding sections of a monitoring site (VSD 7X15)

```
Command Prompt

E:\ARB\1807>township.pl
S.19/T.31S/R.29E          M31S29E19
M30S28E15 M30S28E14 M30S28E13 M30S29E18 M30S29E17 M30S29E16 M30S29E15
M30S28E22 M30S28E23 M30S28E24 M30S29E19 M30S29E20 M30S29E21 M30S29E22
M30S28E27 M30S28E26 M30S28E25 M30S29E30 M30S29E29 M30S29E28 M30S29E27
M30S28E34 M30S28E35 M30S28E36 M30S29E31 M30S29E32 M30S29E33 M30S29E34
M31S28E03 M31S28E02 M31S28E01 M31S29E06 M31S29E05 M31S29E04 M31S29E03
M31S28E10 M31S28E11 M31S28E12 M31S29E07 M31S29E08 M31S29E09 M31S29E10
M31S28E15 M31S28E14 M31S28E13 M31S29E18 M31S29E17 M31S29E16 M31S29E15
M31S28E22 M31S28E23 M31S28E24 M31S29E19 M31S29E20 M31S29E21 M31S29E22
M31S28E27 M31S28E26 M31S28E25 M31S29E30 M31S29E29 M31S29E28 M31S29E27
M31S28E34 M31S28E35 M31S28E36 M31S29E31 M31S29E32 M31S29E33 M31S29E34
M32S28E03 M32S28E02 M32S28E01 M32S29E06 M32S29E05 M32S29E04 M32S29E03
M32S28E10 M32S28E11 M32S28E12 M32S29E07 M32S29E08 M32S29E09 M32S29E10
M32S28E15 M32S28E14 M32S28E13 M32S29E18 M32S29E17 M32S29E16 M32S29E15
M32S28E22 M32S28E23 M32S28E24 M32S29E19 M32S29E20 M32S29E21 M32S29E22
M32S28E27 M32S28E26 M32S28E25 M32S29E30 M32S29E29 M32S29E28 M32S29E27
```

4. References

DWR. Undated. Numbering water wells in California. California Department of Water Resources. Sacramento, CA.

Appendix II.

A Perl program for calculating weekly zone use of MeBr for each monitoring site

1. Notes

The program calculates the weekly zone use of MeBr in various areas (3x3 5x5, 7x7 ... 15x15).

The program calls the subroutine (township.pl) described in Appendix I**.**

2. Source file (mb_use01.pl)

```
#!/usr/local/bin/perl

#    Last change:  LI    1 May 2001    2:02 pm
# mb_use01.pl
# calculates total amount of methyl bromide use in surrounding area of
monitoring sites
# -----------------------------------------------------------

# all parameters are fed from command line
# usage: township.pl MTRS DX,DY
# Please note two forms of MTRS: S.3/T.16S/R.3E or M16S03E03
# The first form was used for arb mornitoring project
# The second for was used in DPR's PUR report
# This program assumes the input in the first format and generates MTRS in the
2nd format



#my ($MTRS, $DX, $DY)= @ARGV;
#print "@ARGV\n";

$working_dir = 'E:\Arb\1807';
chdir $working_dir or die "couldn't find the path $working_dir\n";

$infile1='station.dat';
$infile2='weekly_con.dat';
$infile3='PUR.dat';
#$infile3='PUR_updated.dat';

#$outfile0='weekly_con_use0.dat';
$outfile1='weekly_con_use1.dat';
$outfile2='weekly_con_use2.dat';
$outfile3='weekly_con_use3.dat';
$outfile4='weekly_con_use4.dat';


open IN1, "$infile1";
```

```
open OUT1, ">$outfile1";
open OUT2, ">$outfile2";
open OUT3, ">$outfile3";
open OUT4, ">$outfile4";
open PMS, '>PMS_test.txt';

print OUT1 "ID   County  Station Week    Conc    Appl(1) Appl(2) Appl(3)
Appl(4) Appl(5) Appl(6) Appl(7)\n";
print OUT2 "ID   County  Station Week    Conc    Appl(1) Appl(2) Appl(3)
Appl(4) Appl(5) Appl(6) Appl(7)\n";
print OUT3 "ID   County  Station Week    Conc    Appl(1) Appl(2) Appl(3)
Appl(4) Appl(5) Appl(6) Appl(7)\n";
print OUT4 "ID   County  Station Week    Conc    Appl(1) Appl(2) Appl(3)
Appl(4) Appl(5) Appl(6) Appl(7)\n";


L1: while ($line_IN1 = <IN1>) {
#get the station record
chomp $line_IN1;
($id, $county, $station, $STR1,$total) = split(/\,/,$line_IN1);
print "$id, $county, $station, $STR1, $total\n";



  # skip the title line
  if ($id eq 'ID') {
    next L1;}

  # determine the starting date, number of weeks for air sampling,
  # and the number of days in the first week,

  if ($county eq "Kern"){# for most weeks, sampling usually started from Mon
and ended at Thur
    $num_wk=7;           # However, the first week in Kern county started on
Wendesday, and ended on Thursday.
                         # we assuming that the average of concentration of
these two days represents the average of that week
    $starting_day=201-5; # 201 is the first sampling date in Kern county
(7/19, Wed),
    $days_wk1=2; }       # the julian day for the previous Friday was 201-5.
                         # the day should be shift back 5 days
  else {$num_wk=8;       # In Monterey county, the first sampling date was
Monday(day 255, 09/11).

    $starting_day=255-3; # this number should correspond to 09/08/00, the
first Friday before monitoring started
    $days_wk1=4;}
  $ending_day = $starting_day + 6;

  #get the weekly concentration record
  open (IN2, "$infile2") or die "could not open file $infile2!\n";
   L2: while ($line_IN2 = <IN2>) {
      chomp $line_IN2;
      @wkc= split(/\t/,$line_IN2);
      print "@wkc\n";
      if ($wkc[0] eq $station) {
      last L2;}
     } # end of L2 loop
```

```
  close (IN2);

  # get the weekly application within the specified distances
  for ( $wk=1;$wk<=$num_wk;$wk++)
    {

      for ( $dist=1;$dist<=7 ;$dist++ )
        {
           ($section_ref,$distance_ref) = sub_MTRS($STR1,$dist,$dist);
           @section = @{$section_ref};
           @distance = @{$distance_ref};

           #print "@section\n";
           $num_sec=@section;
           print "$station, $wkc[0], $wk, $dist, $num_sec\n";

           chdir $working_dir or die "couldn't find the path $working_dir\n";

           open (IN3, "$infile3") or die"couldn't open file $infile3\n";

           $weekly_use1[$dist]=0;
           $weekly_use2[$dist]=0;
           $weekly_use3[$dist]=0;
           $weekly_use4[$dist]=0;

           while ($line_IN3 = <IN3>)
            {
             chomp $line_IN3;
             @use = split(/\t/,$line_IN3);
             #print "$use[2], $use[6]\n";

             for ( $l=0;$l<=$num_sec-1;$l++ )
                 {
                    #if ($use[2] eq $section[$l]){
                    if ( ($use[2] eq $section[$l]) and
($use[8]>=$starting_day) and ($use[8]<=$ending_day) ){
                       #$time_factor =
1/(abs($use[8]-($starting_day+$ending_day)/2)+.5);
                       #$dist_factor = 1/($distance[$l]**2);

                       if ($station eq "PMS" &&  $wk==8 && $dist<=3) {
                       print PMS "@use\n";}

                       $delt_t = $use[8]-($starting_day+$ending_day)/2 + 3;
                       #if ( $county eq "Kern" and $wk == 1) {
                       #   @t_factor = (0, 0, 0.1, 0.2, 0.4, 1, 0.85);}
                       #else {
                       #   @t_factor = (0.1, 0.2, 0.4, 1, 1, 0.85, 0.7);}
                       @t_factor = (0.1, 0.2, 0.4, 1, 1, 0.85, 0.7);
                       $time_factor = $t_factor[$delt_t];
                       #print "delt = $delt_t ; t_factor =$time_factor\n";

                       $dist_factor = 1/$distance[$l];

                       $weekly_use1[$dist] += $use[6];
         # no time and dist adjust
                       $weekly_use2[$dist] += $use[6] * $time_factor;
         # time adjust
```

```
                       $weekly_use3[$dist] += $use[6] * $dist_factor;
         # dist adjust
                       $weekly_use4[$dist] += $use[6] * $time_factor *
$dist_factor;     # dist adjust
                       }
                  } #end of for l

            } #end while IN3
            close IN3;
        }  # end for dist

     #print to OUT1 file
     print OUT1 "$id\t$county\t$station\t$wk\t$wkc[$wk]";
     for ($dist=1; $dist<=7; $dist++){
         $weekly_use1[$dist] = int($weekly_use1[$dist]+.5);
         print OUT1 "\t$weekly_use1[$dist]";}
     print OUT1 "\n";

     #print to OUT2 file
     print OUT2 "$id\t$county\t$station\t$wk\t$wkc[$wk]";
     for ($dist=1; $dist<=7; $dist++){
         $weekly_use2[$dist] = int($weekly_use2[$dist]+.5);
         print OUT2 "\t$weekly_use2[$dist]";}
     print OUT2 "\n";

     #print to OUT3 file
     print OUT3 "$id\t$county\t$station\t$wk\t$wkc[$wk]";
     for ($dist=1; $dist<=7; $dist++){
         $weekly_use3[$dist] = int($weekly_use3[$dist]+.5);
         print OUT3 "\t$weekly_use3[$dist]";}
     print OUT3 "\n";

     #print to OUT4 file
     print OUT4 "$id\t$county\t$station\t$wk\t$wkc[$wk]";
     for ($dist=1; $dist<=7; $dist++){
         $weekly_use4[$dist] = int($weekly_use4[$dist]+.5);
         print OUT4 "\t$weekly_use4[$dist]";}
     print OUT4 "\n";


  $starting_day+=7;
  $ending_day = $starting_day + 6;
  } # end for wk

} # end of L1 loop

close IN1, OUT1, OUT2, OUT3, OUT4, PMS;






# ----------------------------------------------------------- #
# usage: sub_MTRS(STR, DX, DY)
sub sub_MTRS {
my ($STR, $DX, $DY) = @_;
my ($MTRS,$LX,$LY, $m, $n, $i, $j, $sx, $sy);
```

```
my ($S, $T_val,$T_dir,$R_val, $R_dir);
my ($SS, $TT_val,$TT_dir,$RR_val, $RR_dir);
my (@new_MTRS);

# extracting section number, township and range for the sampling site
$STR =~ m/S.(\d+)\/T.(\d+)([A-Z])\/R.(\d+)([A-Z])/;
$S=$1;
$T_val = $2;
$T_dir = $3;
$R_val = $4;
$R_dir = $5;

# get the MTRS format for the sampling site
if ( $T_val <=9 ) {$T0_val = "0"."$T_val";} else { $T0_val = $T_val;}
if ( $R_val <=9 ) {$R0_val = "0"."$R_val";} else { $R0_val = $R_val;}
if ( $S <=9 ) {$S0 = "0"."$S";} else{$S0 = $S;}
$MTRS= "M"."$T0_val"."$T_dir"."$R0_val"."$R_dir"."$S0";

#print "$STR\t $MTRS\n";
#print "$S,  $T_val,  $T_dir,  $R_val,  $R_dir\n";

# create a file to store all of the neihbouring MTRS
$LX = $DX*2+1;
$LY = $DY*2+1;
if ( $LX<=9 ) {$LX="0"."$LX";}
if ( $LY<=9 ) {$LY="0"."$LY";}
$mtrs_out = "$MTRS"."($LX".X."$LY)".'.txt';

chdir "$working_dir/temp" or die "couldn't find the path
$working_dir\\temp\n";
open MTRS_OUT, ">$mtrs_out";
open DIST_OUT, ">$dist_out";

# get coordinate for the sampling section
 $n = int($S/6) + 1;
 if($n==1 or $n==3 or $n==5) {
    $m = $n*6 + 1 - $S;}
 else {
    $m = $S - ($n-1)*6;}
 # print "$m, $n\n";

# calculating MTRS for surrounding grids

$k=0;
for ($j=-$DY; $j<=$DY; $j++){
for ($i=-$DX; $i<=$DX; $i++){

        # first, get coordinate for the surrounding sections, also the
township value and range value
        $sx =$m+$i;
        if($sx>6){
            $RR_val = $R_val + int($sx/6);
            $sx=$sx-6*int($sx/6);}
        elsif($sx<1){
             $RR_val = $R_val - (1+abs(int($sx/6)));
             $sx=$sx+6*(1+abs(int($sx/6)));}
        else {
             $RR_val = $R_val;}
```

```
        $sy =$n+$j;
        if($sy>6){
            $TT_val = $T_val + int($sy/6);
            $sy=$sy-6*int($sy/6);}
        elsif($sy<1){
             $TT_val = $T_val - (1+abs(int($sy/6)));
             $sy=$sy+6* (1+abs(int($sy/6)));}
        else {
             $TT_val = $T_val;}

        # The directions for township and range are the same with those of
sampling site
        # Need more analysis here
        $TT_dir = $T_dir;
        $RR_dir = $R_dir;

        # then, get the section number from its xy coordinates
        if($sy==1 or $sy==3 or $sy==5) {
           $SS = $sy*6 - $sx + 1;}
        else {
           $SS = ($sy-1)*6 + $sx;}

        # now, get the MTRS
        if ( $TT_val <=9 ) {$TT_val = "0"."$TT_val";}
        if ( $RR_val <=9 ) {$RR_val = "0"."$RR_val";}
        if ( $SS <=9 ) {$SS = "0"."$SS";}

        #$new_MTRS[$DX+$i+1][$DY+$j+1] =
"M"."$TT_val"."$TT_dir"."$RR_val"."$RR_dir"."$SS";
        #print TEMP_OUT "$new_MTRS[$DX+$i+1][$DY+$j+1] ";

        $new_MTRS[$k] = "M"."$TT_val"."$TT_dir"."$RR_val"."$RR_dir"."$SS";
        $new_DIST[$k] = sqrt($i**2 + $j**2);
        if ( $new_DIST[$k]==0) {$new_DIST[$k] = .5;}
        print MTRS_OUT "$new_MTRS[$k] ";
        print DIST_OUT "$new_DIST[$k] ";
        $k++;


} # end of i loop

#print TEMP_OUT "\n";
#print  "\n";

} # end of j loop

close MTRS_OUT;
close DIST_OUT;
system ("cd ..");
return (\@new_MTRS, \@new_DIST);
} # end of sub
```

3. Output

ID	County	Station	Week	Conc	Appl(1)	Appl(2)	Appl(3)	Appl(4)	Appl(5)	Appl(6)	Appl(7)
1	Mont	SAL	1	1.64	0	6419	15253	36670	56451	56786	60608
1	Mont	SAL	2	2.36	0	0	2253	20970	32288	59092	63540
1	Mont	SAL	3	0.77	0	0	2053	26271	35052	75340	75340
1	Mont	SAL	4	0.5	0	3781	21193	34569	45571	80293	80293
1	Mont	SAL	5	0.7	0	9198	13581	40508	49757	64033	75364
1	Mont	SAL	6	3.01	0	0	14014	40599	46819	80605	90043
1	Mont	SAL	7	1.2	0	0	4652	14618	15787	35316	43891
1	Mont	SAL	8	0.14	0	0	0	0	0	3180	3180
2	Mont	OAS	1	0.38	0	0	0	0	0	0	0
2	Mont	OAS	2	0.44	0	0	0	0	0	0	0
2	Mont	OAS	3	0.17	0	0	0	0	0	0	0
2	Mont	OAS	4	0.4	0	0	0	0	0	0	1330
2	Mont	OAS	5	0.25	0	4730	4730	4730	4730	4730	7376
2	Mont	OAS	6	1.01	0	0	13720	13720	13720	13720	13720
2	Mont	OAS	7	0.39	0	0	0	0	0	0	0
2	Mont	OAS	8	0.08	0	0	0	0	0	0	0
3	Mont	CHU	1	0.73	0	0	2035	2035	2035	5427	5427
3	Mont	CHU	2	1.3	5394	5394	5896	12544	12544	12544	12544
3	Mont	CHU	3	0.34	0	0	0	10185	20330	29551	29551
3	Mont	CHU	4	0.4	4221	4221	17451	19126	31575	31575	31575
3	Mont	CHU	5	0.26	0	0	1968	2064	11317	17912	17912
3	Mont	CHU	6	1.61	0	0	10843	12424	17063	21372	33390
3	Mont	CHU	7	0.59	0	0	4688	4688	4688	4688	4688
3	Mont	CHU	8	0.11	0	0	0	0	0	0	0
4	Mont	LJE	1	10.63	0	0	4551	17133	40244	61116	76506
4	Mont	LJE	2	8.47	0	0	15551	16639	50164	74684	94050
4	Mont	LJE	3	1.27	0	0	13314	16747	37791	63230	82700
4	Mont	LJE	4	1.35	0	0	11441	11876	40179	62182	64253
4	Mont	LJE	5	0.83	0	0	14628	26107	39605	45574	66419
4	Mont	LJE	6	5.63	0	0	9571	17237	32047	40684	55654
4	Mont	LJE	7	2.58	0	0	5822	12468	24938	41870	46994
4	Mont	LJE	8	0.25	0	0	0	0	0	0	0

......

Appendix III

A Perl program for linear regression model and its confidence intervals

1. Source file (linear.pl)

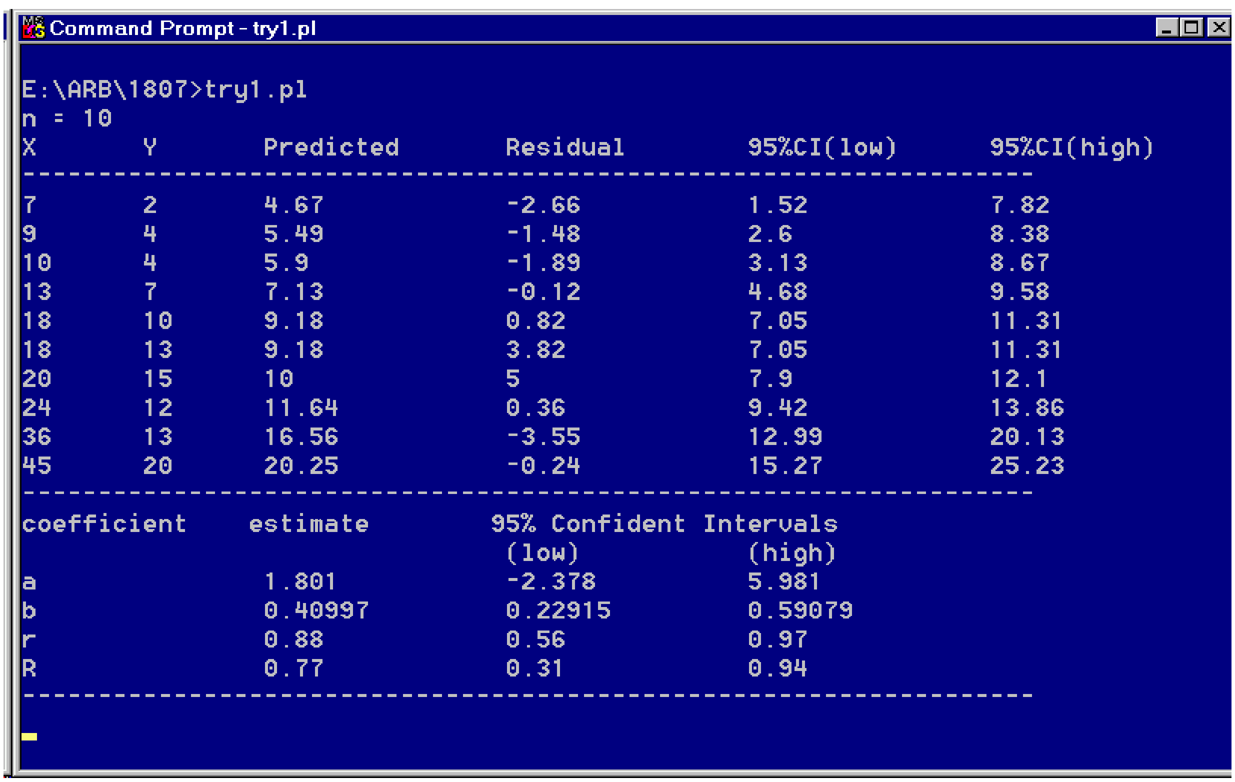
```
#!/usr/local/bin/perl
# Last change:  LI   30 Apr 2001   11:14 am
# linear.pl
# This module accepts (X,Y) pairs of data and does a linear regression: Y = a
+ bX.
# It calculates regression coefficients a, b and correlation coefficient r,
and their Confidence Intervals.
# It predicts Y values and their CIs for each X value.

# The formula and notation are from book "Statistical Methods for the Social
Sciences", P253-273

# testing data set from text book
#@X_array = (2,19,34,40,8,12,20,20,37,19,30,46);
#@Y_array = (48,21,14,11,41,37,22,31,19,42,15,18);
@X_array = (7,9,10,13,18,18,20,24,36,45);
@Y_array = (2,4,4,7,10,13,15,12,13,20);
 $Ref_Xarray = \@X_array;
 $Ref_Yarray = \@Y_array;
sub_Linear($Ref_Xarray, $Ref_Yarray);

# ---------------------------------------------------------- #
sub sub_Linear {
# usage: sub_linear($X_ref, $Y_ref)
my ($X_ref, $Y_ref) = @_;

# look-up table of t values for alfa = 0.050 and 0.025
@t_0050=(0.000, 6.314, 2.920, 2.353, 2.132, 2.015, 1.943, 1.895, 1.860, 1.833,
1.812,1.796, 1.782, 1.771, 1.761, 1.753, 1.746, 1.740, 1.734, 1.729, 1.725,
1.721, 1.717, 1.714, 1.711, 1.708, 1.706, 1.703, 1.701, 1.699, 1.645);

@t_0025=(0.000,12.706, 4.303, 3.182, 2.776, 2.571, 2.447, 2.365, 2.306, 2.262,
2.228,2.201, 2.179, 2.160, 2.145, 2.131, 2.120, 2.110, 2.101, 2.093, 2.086,
2.080, 2.074, 2.069, 2.064, 2.060, 2.056, 2.052, 2.048, 2.045, 1.960);


# read (X,Y) data pairs
@X = @{$X_ref};
@Y = @{$Y_ref};


# initializing variables
$n= @X;
$X_sum =0;
$Y_sum =0;
$XX_sum =0;
$XY_sum =0;

# calculate $a and $b
for ($i=0;$i<=$n-1;$i++)
```

```
{
    $X_sum += $X[$i];
    $Y_sum += $Y[$i];
    $XX_sum += $X[$i]*$X[$i];
    $XY_sum += $X[$i]*$Y[$i];
    $YY_sum += $Y[$i]*$Y[$i];
}

$X_ave = $X_sum/$n;
$Y_ave = $Y_sum/$n;

$b =  ($XY_sum - $X_sum * $Y_sum/$n) / ($XX_sum - $X_sum**2/$n);
$a =  $Y_ave - $b*$X_ave;


# SSE (sum of squared errors), EMS (error mean sqaure) and r, R
$SSE= 0;
$SSX = 0;
$SSY = 0;

for ($i=0;$i<=$n-1;$i++)
{
    $SSE += ($Y[$i]-($a+$b*$X[$i]))**2;
    $SSX += ($X[$i] - $X_ave)**2;
    $SSY += ($Y[$i] - $Y_ave)**2;
}

$Sigma = sqrt($SSE/($n-2));
$SigmaX = sqrt($SSX/($n-1));
$SigmaY = sqrt($SSY/($n-1));

$EMS = $SSE /$n;
$r = ($SigmaX/$SigmaY)*$b;


# confidence interval for regression coefficient b
$Sigma_b = $Sigma / sqrt($SSX);
#$t1 = 2.262;  # the t value is not a constant, should change with df=n-2 and
alfa value
               # in this case, n=11, df =9, alfa = 0.05 (for 95% CI)
               # t_0.025(9) = 2.262 in Page 528
$df = $n-2;
if ( $df >=30 ) { $df=30 ;}
$t = $t_0025[$df];
$b1 = $b - $t * $Sigma_b;
$b2 = $b + $t * $Sigma_b;


for ($i=0;$i<=$n-1;$i++)
{
    $Y0[$i] = $a+$b*$X[$i];
    $DY[$i] = $Y[$i] - $Y0[$i];
    $Y1[$i] = $Y0[$i] - $t*$Sigma*sqrt(1/$n + ($X[$i]-$X_ave)**2/$SSX);
    $Y2[$i] = $Y0[$i] + $t*$Sigma*sqrt(1/$n + ($X[$i]-$X_ave)**2/$SSX);
    $Y0[$i] = int($Y0[$i]*100+.5)/100;
    $DY[$i] = int($DY[$i]*100+.5)/100;
    $Y1[$i] = int($Y1[$i]*100+.5)/100;
    $Y2[$i] = int($Y2[$i]*100+.5)/100;
```

```
}


# confidence interval for regression coefficient a
# obtained by the CI of Y when X = 0 (letting $X[$i] = 0 in above equations)
    $a1 = $a + $b*0 - $t*$Sigma*sqrt(1/$n + (0-$X_ave)**2/$SSX);
    $a2 = $a + $b*0 + $t*$Sigma*sqrt(1/$n + (0-$X_ave)**2/$SSX);

# 95% confidence interval for correlation coefficient r
# see page 271-274 and Table E on page 533
$Tr = 1.151 *log((1+$r)/(1-$r))/log(10); # In Perl log(expr) returns natural
logarithm of expr;
$SigmaT = 1/sqrt($n-3);                  # logX = lnX/ln10
$Tr1 = $Tr - 1.96 * $SigmaT;
$Tr2 = $Tr + 1.96 * $SigmaT;

$r1 = (10**($Tr1/1.151)-1) / (10**($Tr1/1.151)+1);
$r2 = (10**($Tr2/1.151)-1) / (10**($Tr2/1.151)+1);

$R = $r**2;
$R1 = $r1**2;
$R2 = $r2**2;

if ( $r1<0 and $r2>0){
     if ($R1>$R2) {$R2 = $R1;}
     $R1=0;
   }
if ($r1<0 and $r2<0){
    $tmp = $R2;
    $R2 = $R1;
    $R1 = $tmp}


# need to convert Tr1 and Tr2 from table E on page 533 to r1 and r2

# formating for print
$a = int($a*1000+.5)/1000;
$a1 = int($a1*1000+.5)/1000;
$a2 = int($a2*1000+.5)/1000;

$b = int($b*100000+.5)/100000;
$b1 = int($b1*100000+.5)/100000;
$b2 = int($b2*100000+.5)/100000;

$Tr = int($Tr*100+.5)/100;
$Tr1 = int($Tr1*100+.5)/100;
$Tr2 = int($Tr2*100+.5)/100;

$r = int($r*100+.5)/100;
$r1 = int($r1*100+.5)/100;
$r2 = int($r2*100+.5)/100;
$R = int($R*100+.5)/100;
$R1 = int($R1*100+.5)/100;
$R2 = int($R2*100+.5)/100;


# print original data pairs and analysis results
print "n = $n\n";
```

```
print "X\tY\tPredicted\tResidual\t95%CI(low)\t95%CI(high)\n";
print "-------------------------------------------------------------------\n";
for ( $i=0;$i<=$n-1;$i++)
{
    print "$X[$i]\t$Y[$i]\t$Y0[$i]\t\t$DY[$i]\t\t$Y1[$i]\t\t$Y2[$i]\n";
}
print "-------------------------------------------------------------------\n";
print "coefficient    estimate        95% Confident Intervals\n";
print "                                (low)           (high)\n";
print "a\t\t$a\t\t$a1\t\t$a2\n";
print "b\t\t$b\t\t$b1\t\t$b2\n";
#print "Tr\t\t$Tr\t\t$Tr1\t\t$Tr2\n";
print "r\t\t$r\t\t$r1\t\t$r2\n";
print "R\t\t$R\t\t$R1\t\t$R2\n";
print "-------------------------------------------------------------------\n";
$e = <>;

print OUT  "$a\t\t$a1\t\t$a2\t \t$b\t\t$b1\t\t$b2\t \t$R\t\t$R1\t\t$R2\n";
#print "$X_sum\t$Y_sum\t$XX_sum\t$XY_sum\n$Sigma\n";

} # end of sub
```

2. Example



```
Command Prompt - try1.pl

E:\ARB\1807>try1.pl
n = 10
X       Y       Predicted       Residual        95%CI(low)      95%CI(high)
-------------------------------------------------------------------
7       2       4.67            -2.66           1.52            7.82
9       4       5.49            -1.48           2.6             8.38
10      4       5.9             -1.89           3.13            8.67
13      7       7.13            -0.12           4.68            9.58
18      10      9.18            0.82            7.05            11.31
18      13      9.18            3.82            7.05            11.31
20      15      10              5               7.9             12.1
24      12      11.64           0.36            9.42            13.86
36      13      16.56           -3.55           12.99           20.13
45      20      20.25           -0.24           15.27           25.23
-------------------------------------------------------------------
coefficient    estimate        95% Confident Intervals
                                (low)           (high)
a               1.801           -2.378          5.981
b               0.40997         0.22915         0.59079
r               0.88            0.56            0.97
R               0.77            0.31            0.94
-------------------------------------------------------------------
```

References

Agresti Finlay, 1986. Statistical Methods for the Social Sciences, 2nd Edition, Dellen Macmillan. P253-273.